

(NASA-CR-161115) AEROSOL AND NUCLEATION N79-18511  
RESEARCH IN SUPPORT OF NASA CLOUD PHYSICS  
EXPERIMENTS IN SPACE Final Report (Wyoming  
Univ.) 90 p HC A05/MF A01 CSCI 04A  
63/46 16083



DEPARTMENT OF  
**ATMOSPHERIC  
SCIENCE**

College of Engineering  
University of Wyoming, Laramie

FINAL REPORT

Contract No. NAS8-32067

AEROSOL AND NUCLEATION RESEARCH  
IN SUPPORT OF NASA CLOUD PHYSICS  
EXPERIMENTS IN SPACE

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NASA CLOUD PHYSICS EXPERIMENTS IN SPACE

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AEROSOL AND NUCLEATION RESEARCH IN SUPPORT OF  
NASA CLOUD PHYSICS EXPERIMENTS IN SPACE

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## 1. INTRODUCTION

The tasks of this research contract have been identified in Exhibit A of the contract as:

- Task 1 - Establish the impact of ACPL scientific functional requirements on ice nuclei generation and characterization subsystems.
- Task 2 - Conduct detailed evaluations of potential aerosol generating systems with special emphasis on reliability, repeatability and general suitability for application in Spacelab.
- Task 3 - Examine possible contamination problems associated with aerosol generation techniques.
- Task 4 - Determine the ice nucleating abilities of candidate test aerosols and evaluate the possible impact of impurities on the nucleating abilities of those aerosols.
- Task 5 - Evaluate the relative merits of various methods of aerosol size and number density measurements.

The main purpose of the work was to develop an ice nucleus generator which, within the facility concept of the ACPL, would provide a test aerosol suitable for a large number and variety of potential experiments. No quantitative specifications were set prior to commencing the research work. The spirit of the effort was to try for the best performance in all regards, bearing in mind the need for simplicity, ease of operation, small size and relatively low cost.

We interpreted the requirements for the generator in the following terms:

1. The generator must have reproducible, predictable output with a minimum of variability.
2. The generating system should be simple and easy to operate.
3. It should have small requirements for power, weight and additional apparatus.
4. It should not produce any material other than the desired aerosol in significant quantities (such as gaseous byproducts or heat).

5. It should present no safety hazard.

The desirable characteristics of the produced aerosol were taken to be:

1. Temperature range of nucleating activity such that active nuclei can be found from the warmer temperatures (warmer than  $-5^{\circ}\text{C}$ ) to the colder end of the nucleus spectrum ( $-20^{\circ}\text{C}$ ).
2. Fairly well known chemical characteristics.
3. Range of sizes of active particles from about  $.01$  to  $1\ \mu\text{m}$ .
4. Particle shape close to spherical so that particle size and diffusion characteristics are predictable.

The basic testing procedures for selection were quite straightforward: particles were generated, the size spectrum was determined, and the aerosol was tested for its ice nucleating ability.

A wide variety of generating methods was investigated. These are described in greater detail later in this report. The techniques used were:

- evaporation of a nebulized aqueous suspension of AgI particles formed by precipitation from solution
- evaporation of a nebulized solution of  $\text{AgI-NH}_4\text{I}$  complex
- condensation of AgI vapors within a heated quartz tube
- condensation of AgI vapors produced from a heated nichrome wire which is plated with AgI (the Barchet generator)
- evaporation of monodisperse solution droplets of AgI produced by vibrating orifice generator (the Berglund-Liu generator)

Of these different generating methods, the one which best fulfills the requirements is the first one listed. This generator is recommended for use by the ACPL. It is described in greater detail in a later section of this report.

In the course of this research, two instrumentation and aerosol characterization workshops were conducted, the first one in Reno, Nevada, at the

of Wyoming. The details of the experiments and their results are elaborated later in this report.

## II. INSTRUMENTATION AND LABORATORY FACILITIES

### A. Aerosol Size Spectra

The Wyoming Aerosol System consisted of a group of three instruments and incorporated a computer controlled data system (see Fig. 2.A.1). The three instruments are:

1. Aitken Nucleus Counter (Environment One, Model Rich 100),
2. An Electrical Aerosol Analyzer (Thermo Systems, Model 330),
3. An Optical Particle Counter (Climet Optics and in-house electronics).

The Aitken nucleus counter is of the expansion chamber type, with light attenuation used for determining the cloud density. The electrical mobility analyzer has been described by Liu, et al. (1973) and by Liu and Pui (1975). An optical particle counter very similar to the one we used has been described by Husar (1974).

The Aitken counter was operated in its standard form and measured the total particle concentration of particles larger than about  $0.03 \mu\text{m}$  (Walter and Jaenicke, 1973). The other Aitken counter which was frequently used was a Gardner counter (Gardner Associates, Inc., Type CN).

The mobility analyzer (EAA) was operated under computer control, the precipitating voltage being incremented in eleven steps of decreasing duration and with averaging performed during the later part of each step. The calibration of Liu and Pui (1975) was assumed to apply. It is evident from the data that measurements in the first one to three steps (smallest particle sizes) were



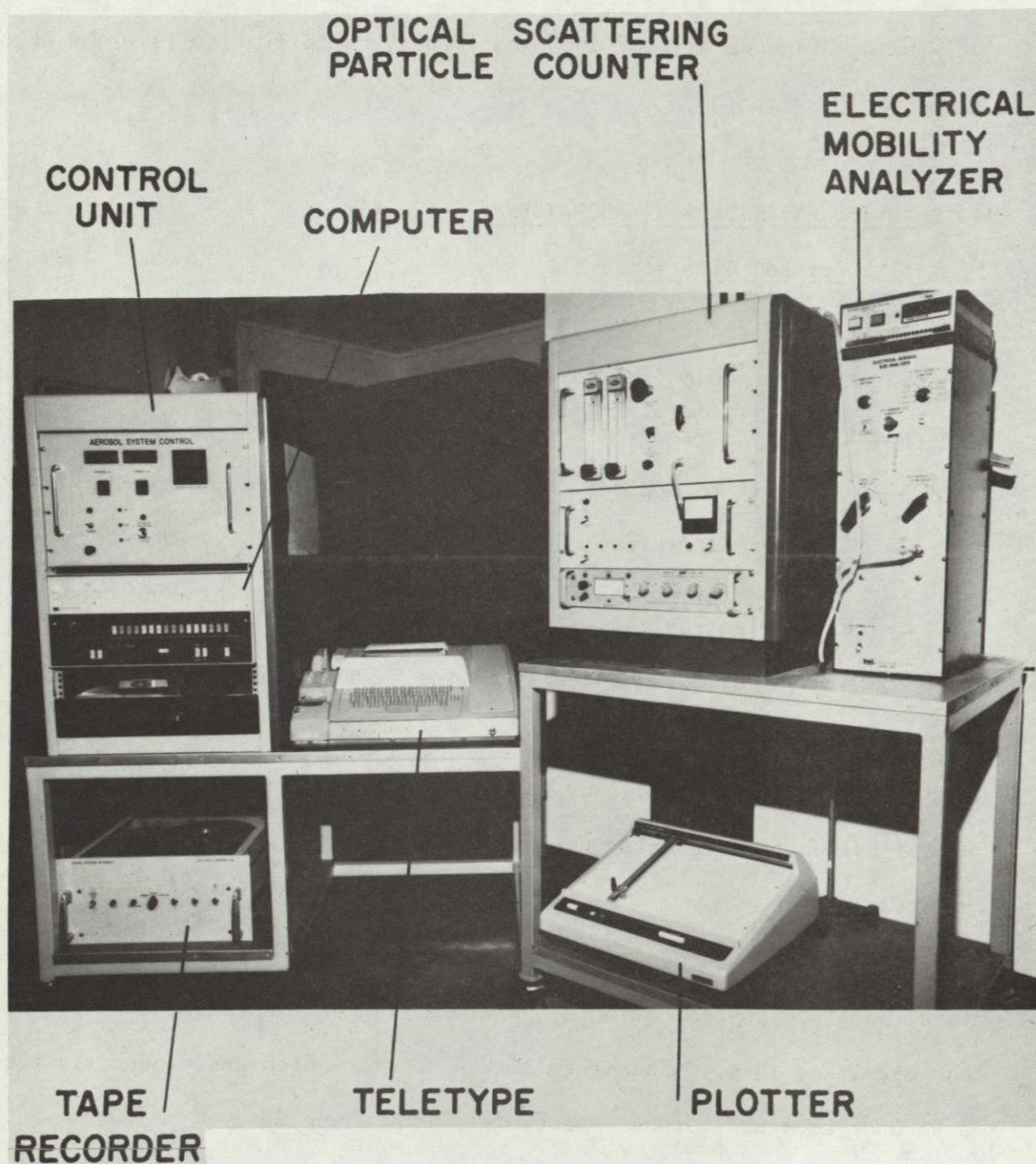


Fig. 2.A.1: Aerosol Monitoring System.

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unreliable, as was also found by other users of the instrument (private communications). The range over which the data are incorrect appears to be somewhat variable with aerosol type and can only be judged from the shape of the resulting spectra. Also, erroneous data are obtained if the aerosol is changing during the sampling period, or if the aerosol concentration is so low that the measurements are disturbed by noise. Because of these problems, it is difficult to assign accuracy limits to the observed size distributions. From our experience the data are most reliable over the size range 0.03 to 0.3  $\mu\text{m}$ .

The optical particle counter was operated in the standard configuration recommended by the manufacturer except for the tailor-made signal processing circuitry. The pre-amplified photomultiplier output was calibrated against particle size using monodisperse latex, salt and dye particles. Pulses from the photomultiplier were filtered for pulse width, and sorted by pulse height into 6 categories; the counting was performed by the computer.

At the end of each sample cycle the size distribution was calculated by the computer in differential form. The results were then printed in tabular form by a teletype terminal and a graphical plot was produced with an X-Y plotter. The complete cycle for producing a size distribution required 214 sec, and the volume sampled was about 37 liters.

It should be recognized that while the size distributions are presented in terms of particle diameter, the meaning of such equivalent diameters for nonspherical particels (and especially for chain-like aggregates) is by no means straightforward. The matter is complicated even further by the fact that the three instruments in the aerosol sizing system respond to different



characteristics of aerosol particles. In the face of these uncertainties it is reassuring to find that the observed aerosol spectra join smoothly at the boundaries of the size ranges covered by the instruments.

#### B. Deposition Nuclei Measured by the Membrane Filter Processor

The thermal gradient diffusion chamber operated by the University of Wyoming is similar in principle to the instruments described by Bigg et al. (1963) and by Gagin and Aroyo (1969). The diffusion chamber was used for the activation of nuclei caught on membrane filters. The operating principle of the diffusion chamber is to maintain the samples at a fixed temperature on the lower plate of the chamber while an ice surface located a small distance above the lower plate is held at a slightly warmer temperature, thus providing the vapor source for the activation and growth of ice crystals. Supersaturation is calculated from the difference in temperature between the two plates. The chamber is further enclosed by a cold box which serves as the heat sink and which excludes the possibility of interference by vapor sources at higher temperatures from the surroundings of the chamber.

The construction of the diffusion chamber is shown in cross section in Fig. 2.B.1 and a photograph of the complete instrument is shown in Fig. 2.B.2. The lower plate actually consists of two parts, an upper layer which is removable from the chamber for the loading and unloading of filters, etc, and a lower layer in which the heater is embedded. The entire lower plate can be moved horizontally from the position under the ice layer to beneath the observation windows for examination of the activated crystals. The "box" enveloping the chamber is kept several degrees colder than the desired



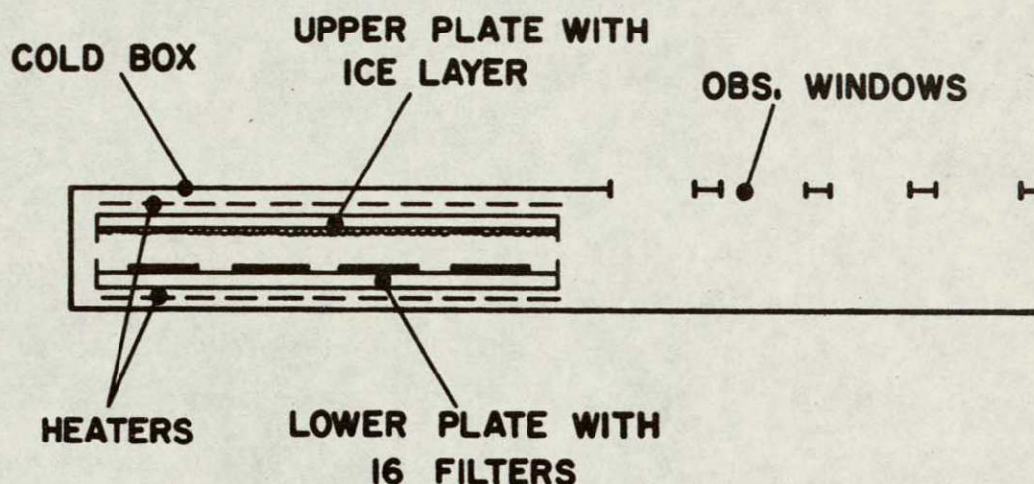
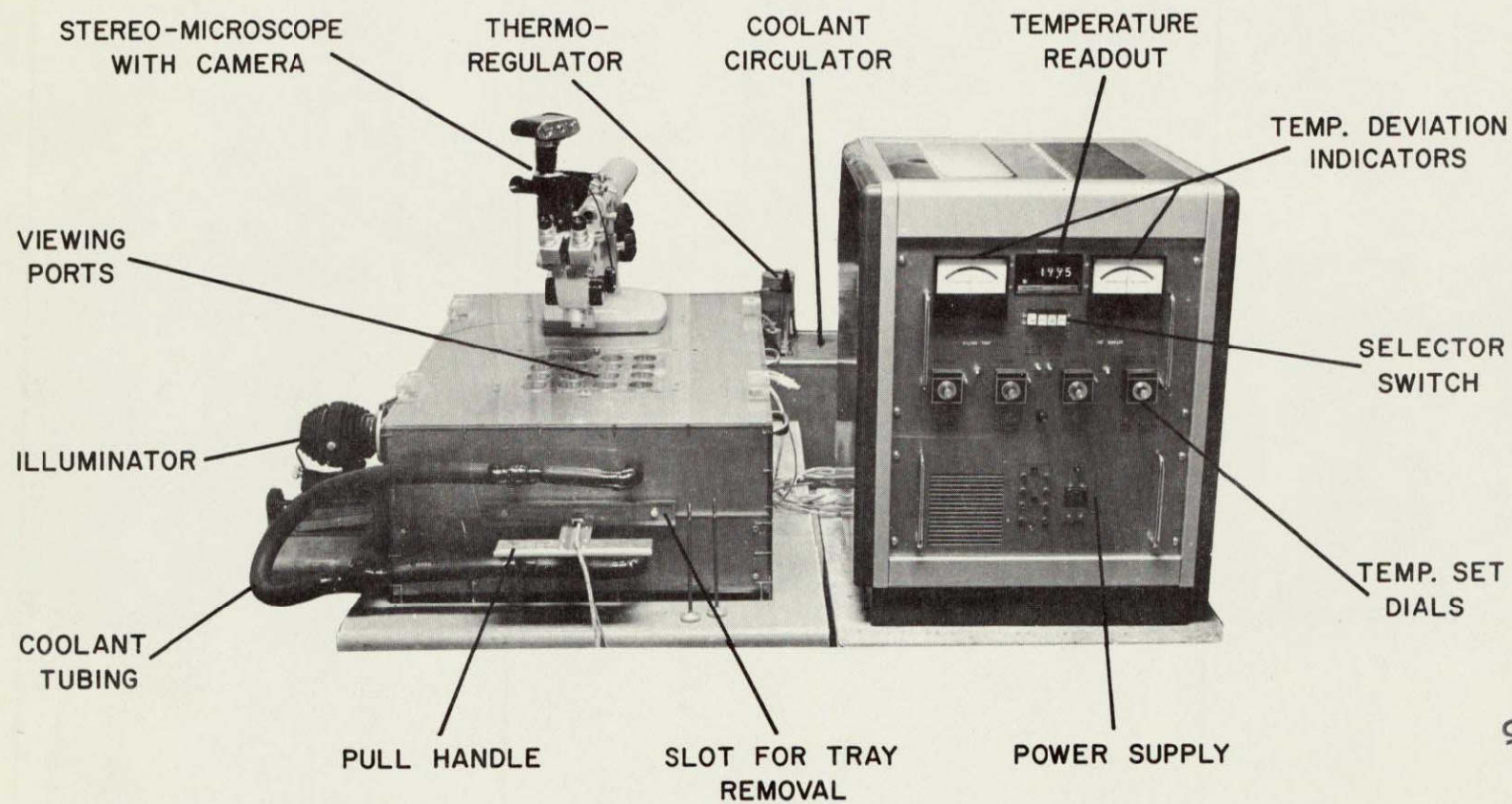


Fig. 2.B.1: Cross section of membrane filter processor.

operating temperature. The temperatures of the lower plate and of ice surface are controlled by heating grids embedded between the plates and the box. The box itself is cooled by a circulating refrigerant. Temperature sensors are embedded as near to the surface of the upper and lower plates as possible. The sensors are connected to the electronic control unit which in turn regulates the power applied to the heater grids.

The ice surface is prepared by lifting off the upper half of the chamber and by freezing a thin layer of water onto the upper plate. A new ice layer is prepared once a week during routine operation of the chamber, at the same time the chamber is also completely cleaned.





FILTER PROCESSING SYSTEM

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### C. Contact-Freezing Nucleation Measured by the DFC Instrument

The basic concept of the contact-nucleus counting instrument (or drop freezing counter, DFC) is to force aerosol particles into contact with supercooled drops of clean water and to observe the individual freezing events which result. The supercooled drops, which are to serve as detectors, are supported on a cold stage whose temperature is controlled. Aerosol particles are deposited onto the drops by electrostatic precipitation.

With the contact being enforced, rather than depending on diffusion or aerodynamic capture, the sizes of the detector drops are only of indirect consequence, and there is no need to account for the complex processes which normally influence the coagulation of aerosol particles with cloud droplets. Because of the need to detect the freezing of each drop when it occurs, relatively large (about 2 mm diameter) drops are used. High purity water is used to form the drops, since nucleation by particles suspended in the drops should not occur until temperatures much colder than the intended test temperature.

The design of the instrument is schematically represented in Fig. 2.C.1. A cold plate supports the drops and forms the bottom plate of a precipitator chamber. The precipitator is a modified form of a commercial unit (Thermo-Systems, Inc., Model 3100). Aerosols are drawn into the chamber and are given a small charge by diffusive attachment of small positive ions. Subsequently, as the carrier air moves along the chamber (with a velocity of  $19 \text{ cm} \cdot \text{sec}^{-1}$ ) aerosol particles are forced into contact with the water drops by pulse-wise application of a positive voltage (4,200 V) to the top electrode plate. The magnitude of the particle charges varies with particle

size: the mean charge on  $0.1\ \mu\text{m}$  particles is about 8 elementary charges, and on  $1\ \mu\text{m}$  particles it is 40 elementary charges. The fraction of particles which get charged decreases with decreasing particle size and becomes quite small below  $0.01\ \mu\text{m}$  particle diameter. Consequently, aerosol collection takes place with incomplete efficiency. Details of the operation of the charger and precipitator were given by Liu, Whitby and Yu (1967).

The electric field does not in itself cause freezing of the target drops, as is evident from the experiments of Doolittle and Vali (1975). Ions attached to the aerosol particles can, in principle, modify the nucleating abilities of the particles. In view of the smallness of the charges, and the fact that only 0.01% or less of the surface area of the particles is covered by ions, it is not considered likely that nucleating ability is in fact altered. There is no indication in the literature that influences due to charges should be expected under the conditions encountered in the instrument. Gabarashvili and Glikl (1967) reported enhanced nucleation on charged naphthalene and cholesterol particles but they were dealing with  $10^6\ \mu\text{m}^{-2}$  elementary charges on the particle surfaces whereas the corresponding number in the DFC instrument is about  $10^2\ \mu\text{m}^{-2}$ . It can also be argued that the presence of charges on nuclei within the instrument is not unrealistic, as atmospheric aerosol particles also carry charges, although usually those charges are smaller.

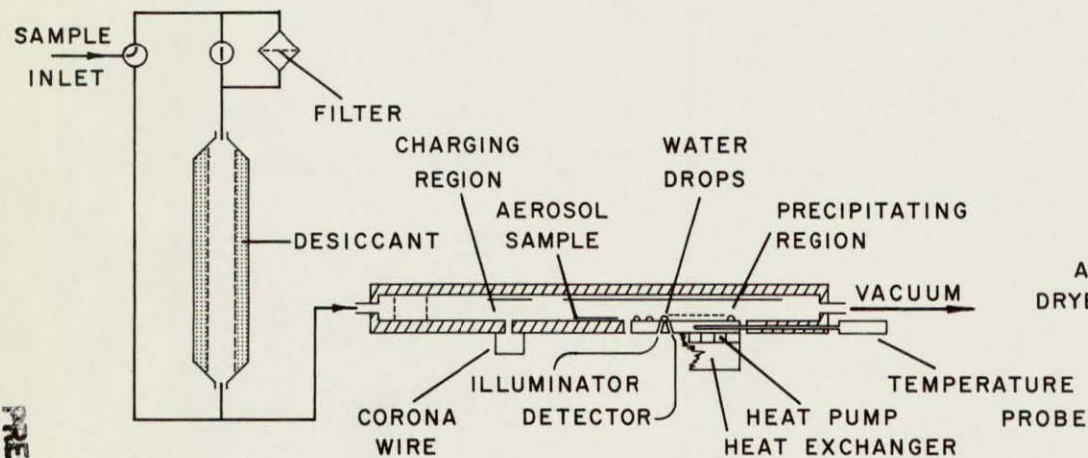
The cold stage holds 75 drops. Illuminator and detector optical fibers are embedded in the stage underneath each of the drops. Illumination is provided for all drops by a single incandescent source. A separate photoresistor is used as detector for each drop. The fibers are so arranged underneath

the drops that, if the drops are properly positioned with respect to the fibers, no light is reflected to the detectors as long as the drops remain liquid. Upon freezing, the opacity of the drops increases and light is reflected to the detectors. This increase in light triggers the counting, display and recording circuits. There is about a 5-20 sec response time (depending on temperature) associated with this technique of detection due to the time it takes for a sufficient amount of ice to freeze in the drops following nucleation.

To prevent the drops from freezing due to nucleation by the supporting surface, the cold stage is covered with a mylar film of 0.01 mm thickness, the film being further coated with a silicone varnish (General Electric DF-88, or equivalent).

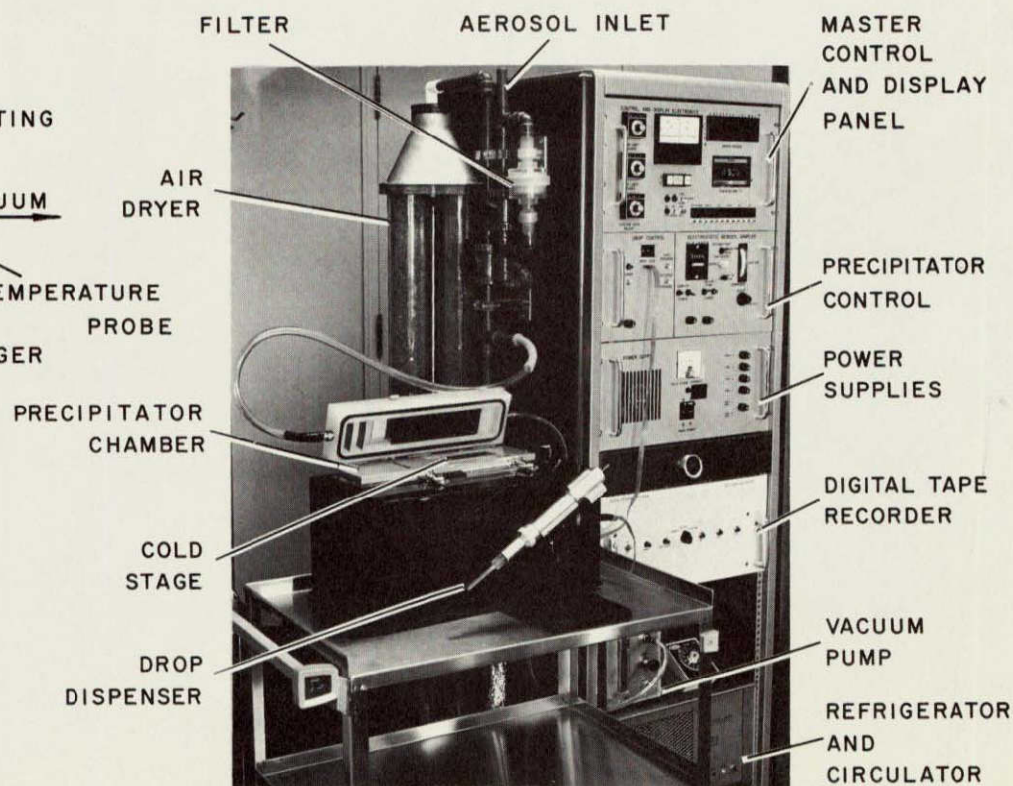
The dew point of the sample air must be below the temperature at which the measurements are made to avoid the formation of frost between the drops. A diffusion dryer is used for samples carried in moist air. The dryer is not used for artificial aerosols prepared with dry air, or for natural air samples when the dew point temperature is below the test temperature, with the dryer the dew point is lower to about  $-25^{\circ}\text{C}$ . To minimize drop evaporation, the optimum operating condition would be to have the dew point of the carrier air only slightly below the operating temperature, but the humidity control necessary for this has not yet been added to the instrument. A photograph of the complete instrument is also shown in Fig. 2.C.1.

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# DFC (DEPOSITION/FREEZING/CONTACT) ICE NUCLEUS COUNTING SYSTEM

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#### D. The Settling Cloud Chamber (SCC)

The product of this research effort, the ice nucleating aerosol, will ultimately be used in the cloud chamber of the ACPL. The three previously described instruments perform rather selective and quantitative measurements, but none of them were designed to reproduce the conditions found in a cloud chamber. In order to perform some measurements of the nucleating activity in a cloud chamber environment, we modified an existing flow-through type chamber (NCAR acoustical counter, Langer, 1973) into a static chamber similar to Ohtake's (1976). A photograph of this device appears in Fig. 2.D.1. The modifications consisted of removing the airflow lines and plugging the chamber outlet at the bottom of the chamber. The top of the cylindrical chamber was extended and covered with a removable transparent plastic lid; it provides access to the chamber for growing the cloud, injecting the aerosol and placing the sugar tray. The sugar tray holds a supercooled sugar solution in the bottom of the chamber; ideally, all small ice crystals which form in the chamber settle to the tray and grow to macroscopic size for counting. The cloud is formed in the top of the chamber when a warm, wet sponge is inserted in place of the lid.

The experimental procedure involves cooling the chamber and sugar tray to the selected temperature (measured by a thermistor or thermocouple) and injecting the aerosol sample. Next the cloud is formed, and after about two minutes, the sponge is removed and the lid replaced. After a waiting period of about five minutes (for crystal fallout and growth), the tray is removed and the crystals are counted.



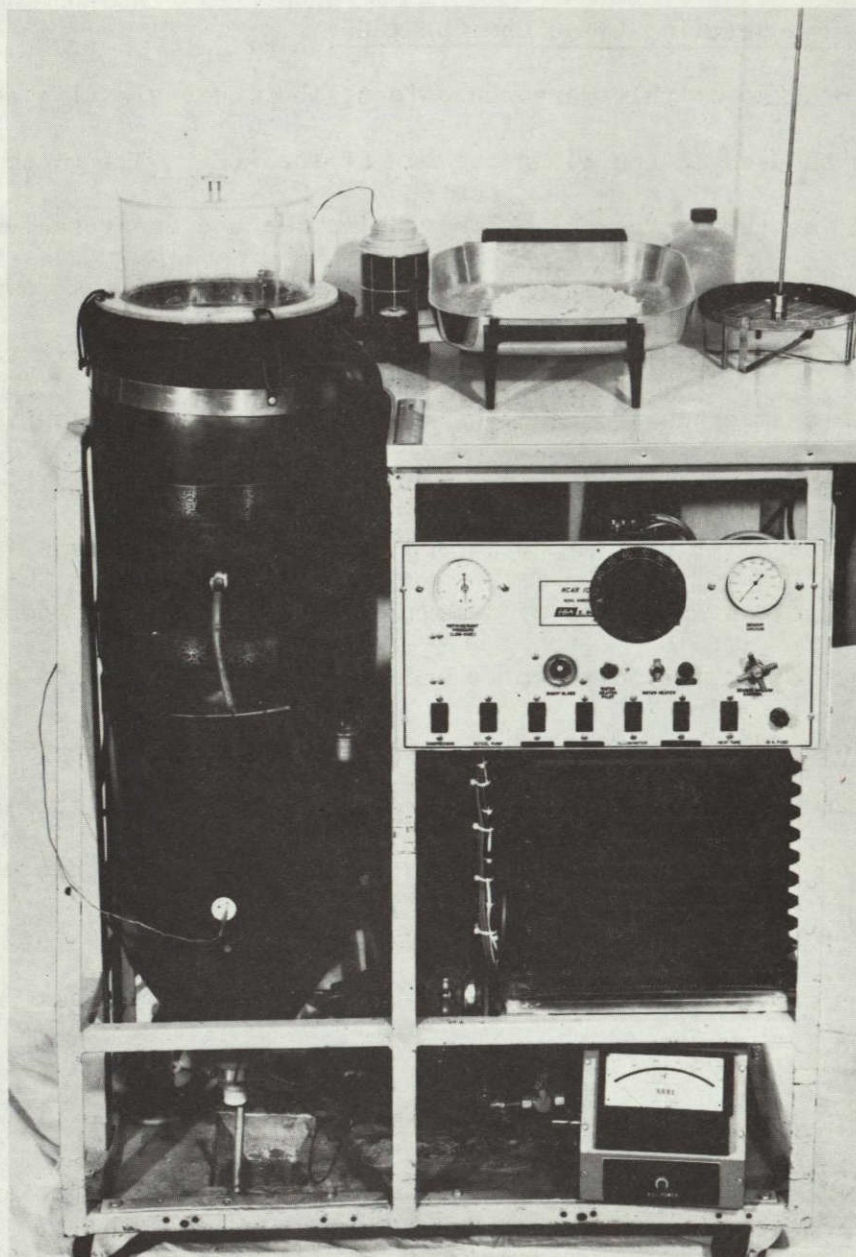


Fig. 2.D.1: Settling Cloud Chamber (SCC) Instrument.

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There were inherent difficulties with the cloud chamber that made quantifying the results tenuous. Among these problems were: the sensitivity of the sugar solution, the dependence of a nucleation event upon the cloud droplet concentration, and the existence of temperature gradients and convection within the chamber. Therefore, the settling cloud chamber was used primarily to confirm the activity in a cloud chamber environment and not to make quantitative measurements.

#### E. The CCN Chamber

During the Laramie workshop, several CCN measurements were made on both NaCl and AgI aerosols for the purposes of aerosol characterization and instrumental comparison. The Wyoming CCN chamber is a horizontal parallel plate static thermal gradient diffusion chamber. The plate separation is 1.0 cm and the aspect ratio is 8. Temperature control is accomplished with thermistor sensors, an amplifying circuit and thermoelectric coolers on the bottom plate. The sample is brought to the temperature of the top plate in a pre-conditioning chamber which is connected with the top plate and an isothermal bath circulator. Droplet detection is accomplished photographically with a 35 mm camera and off-axis laser illumination. The sample volume is about 37 mm<sup>3</sup>. The device is described in greater detail, and calibration procedures are outlined, in Lukow (1977).



### III. SELECTION OF ICE NUCLEANTS AND MEASURES OF ACTIVITY

There is a very large variety of artificial ice nucleating material. The requirement of having a fairly warm threshold temperature narrows the list to just a few candidates, including silver halides, organic nucleants (Fukuta, 1966) and biogenic materials (Schnell, 1974). Further narrowing of the list was imposed by both time constraints (insufficient time to test all possible candidates) and invoking some of the aerosol requirements. For example, the organic nucleants have substantial vapor pressures (compared to the other materials) at temperatures ranging down to ice nucleating experiment temperatures (say,  $-5^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$ ). Thus the organic nucleants would pose a gaseous contamination problem for the cloud chamber. The biogenic materials suffer from being rather large in size (larger than about  $0.2\text{ }\mu\text{m}$  to  $0.45\text{ }\mu\text{m}$  according to Schnell, 1974) which is larger than desirable. Thus the selection was narrowed to the silver halide compounds. Of these, silver iodide (and complexes thereof) has received the most attention in the literature and the widest use in weather modification activities. The natural choice for these experiments was silver iodide and complexes of silver iodide.

The water affinity and nucleating ability of silver iodide can be strongly affected by the method of preparation and by the addition of complexing agents. "Pure" silver iodide, which can be generated using gaseous reaction and heating technique (Corrin, et al. 1971), is hydrophobic and actually quite a poor nucleating material (threshold activation temperature of about  $-10^{\circ}\text{C}$ ). In comparison, complexes of silver iodide with ammonium iodide are hygroscopic and possess rather good nucleation temperatures, with the warmest activity near  $-10^{\circ}\text{C}$  (Davis et al., 1975 and Reischel, 1976).

Measurements of the ice nucleating activity of the various aerosols depend to a large degree upon the manner in which they are tested, i.e., the device and operating conditions. This aspect is in addition to the characteristics of the nucleating material that tend to favor certain nucleation modes. For example, the cloud droplet concentration has an important influence upon the number of ice crystals which form by contact nucleation in a cloud chamber. Furthermore, the activity measured in one device (e.g., the filter processor) can not be readily compared with that measured in a different device (e.g., the drop freezing counter), and predicting the activity in a cloud chamber environment from measurements in two different devices may be very difficult. For these reasons, we chose to measure the nucleating activity using the wide variety of instruments which were available in order to more completely characterize the aerosols.

The results of the nucleation measurements are presented in several different ways. This multiplicity is necessary because several distinct modes of nucleation were tested and because it allows easier comparison among the different aerosols. The following definitions apply:

FRACTION ACTIVE - the number of ice nuclei active under the specified conditions divided by the total number of aerosol particles in the same sample.

ICE NUCLEI CONCENTRATION - the number of ice nuclei active under the specified conditions divided by the volume of carrier gas (air or nitrogen); all concentrations were corrected for dilution so that the reported concentration refers to the output directly from the generator (or directly from the EC in the case of a classified aerosol). This is consistent with our reporting of the aerosol concentration at the same location.

CLASSIFIED AEROSOL - an aerosol with size distribution altered after primary generation by utilizing some characteristic of the particle size (such as mobility). Several devices were used to obtain a classified aerosol, namely, the EC, the EAA and a cascade impactor.

Typical activities of ice nucleating materials are quite sensitive to temperature, such that no nucleation occurs above some threshold temperature and nucleation at colder temperatures is a rapidly increasing function. Thus, when the activity (FRACTION ACTIVE or CONCENTRATION) is measured as a function of temperature, an ice nucleus SPECTRUM results.

#### IV. GENERATING METHODS TESTED: PROCEDURES AND RESULTS

As mentioned earlier, many different techniques and materials were tested, resulting in several disappointing or failure experiments and also several very promising experiments. The best aerosol generating system and nucleating material within the limitations and requirements of the ACPL was the evaporation of a nebulized aqueous suspension of AgI particles formed by precipitation from solution. Naturally this technique received the greatest amount of our attention and the greatest number of detailed tests to determine its reproducibility and the size and nucleating characteristics. This technique is described here first, with other, less encouraging techniques following.

A. Evaporation of a Nebulized Aqueous Suspension of AgI Particles Formed by Precipitation from Solution.

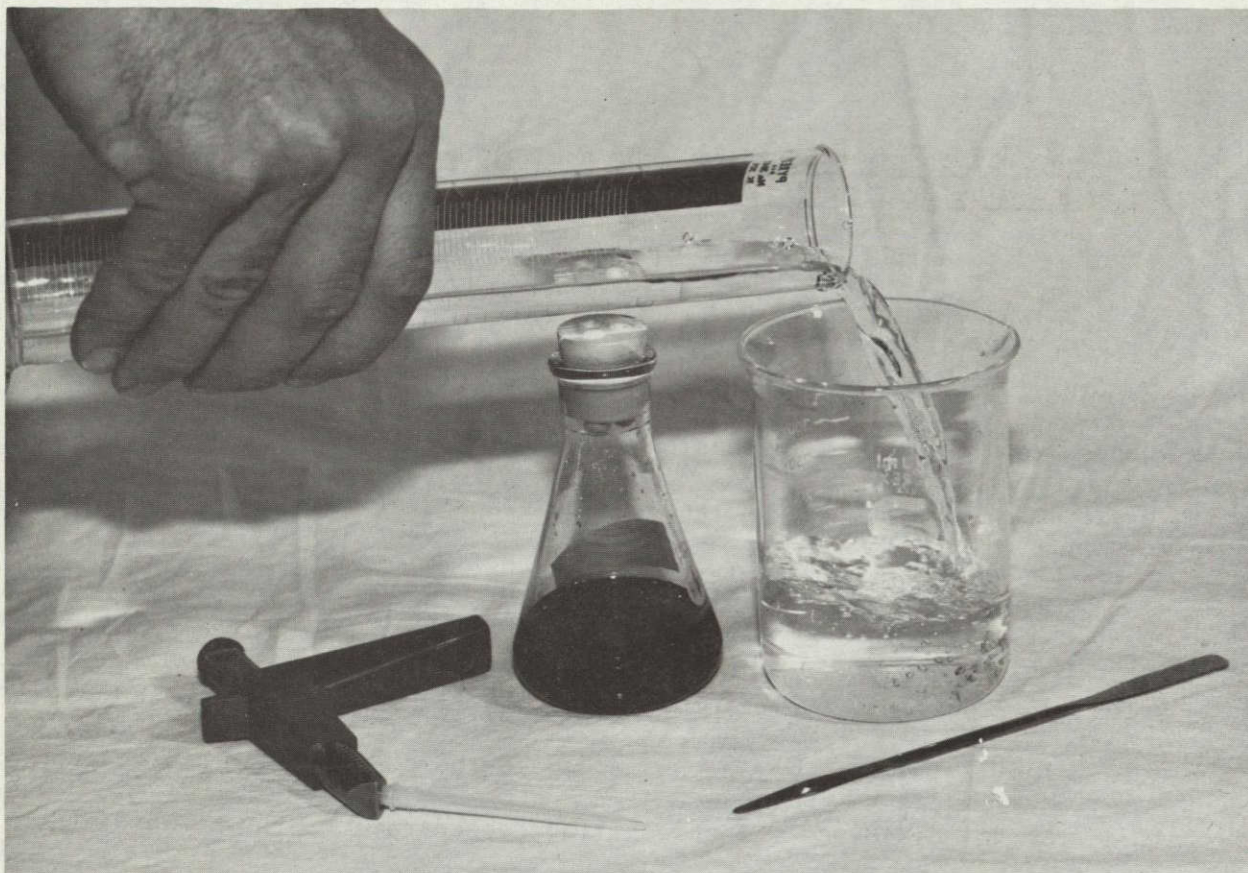
1. Procedure for generation.

The chemicals used for generating the AgI suspension were of reagent grade purity. The water used for preparing initial solutions and for the final generation of the AgI suspension was singly distilled in a Corning Ac-1b glass laboratory still and then de-ionized and filtered by a Millipore Milli-Q system. The distilled water has a conductivity of 10  $\mu\text{mho}$ .

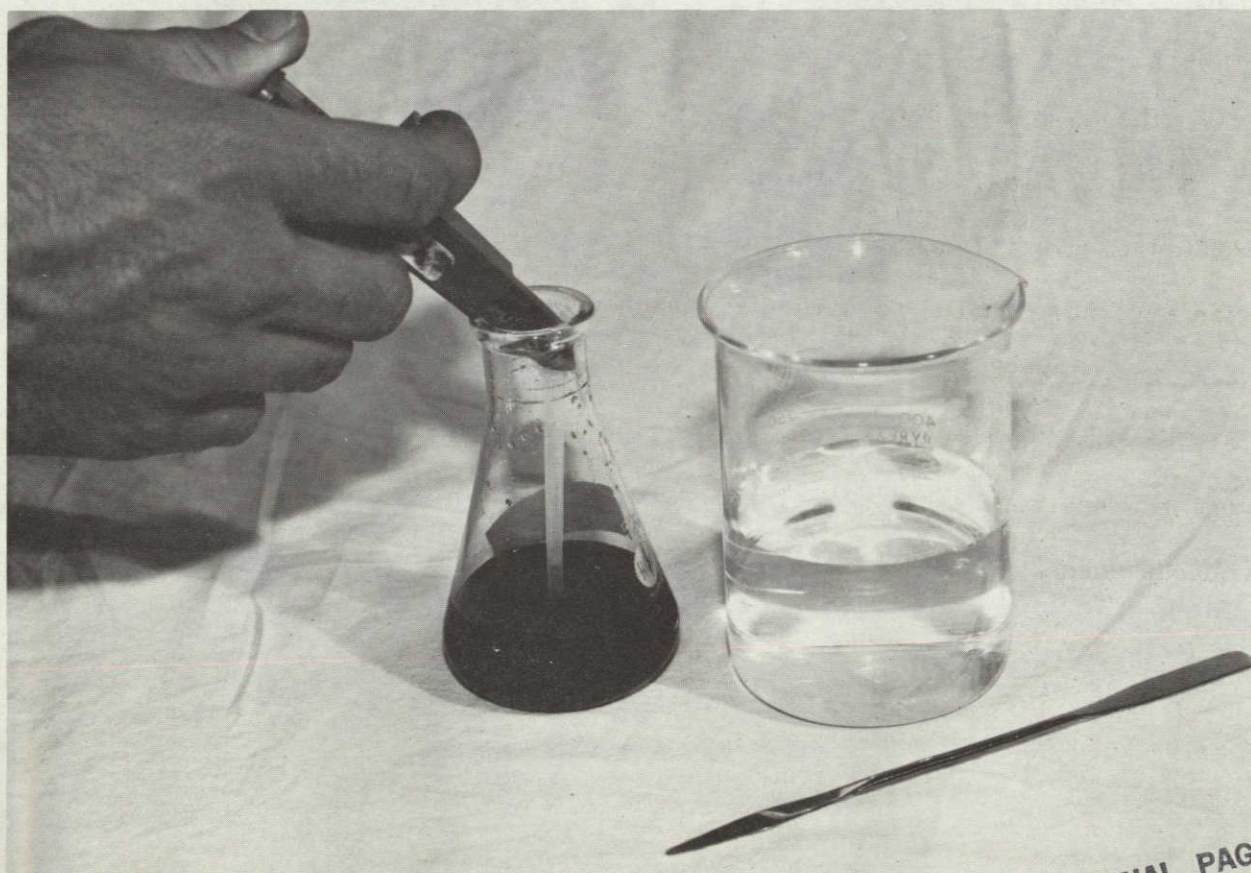
The initial  $\text{NH}_4\text{I}$ -AgI complex solution was prepared by first dissolving 0.25 moles (36.3256 g) of  $\text{NH}_4\text{I}$  in 2.78 moles (50 ml) of distilled water. Then 0.10 moles (23.4774 g) of AgI was added to the solution and stirred until all of the AgI dissolved. The resulting concentrated solution was translucent and brownish in color. The solution was stable over a several month period (which would allow it to be mixed on the ground for later use in the ACPL).

The following description of the generation of the AgI suspension can be aided by Figs. 4.A.1a. through 4.A.1d. The procedure begins with pouring 200 ml of distilled water into a container (Fig. 4.A.1a.). Next, 0.05 ml of the  $\text{NH}_4\text{I}$ -AgI complex solution is measured out using a micropipette (Fig. 4.A.1b) and squirted into the distilled water (Fig. A.4.1b). This immediately produces a momentary supersaturation with respect to AgI which causes AgI to precipitate out. The suspension is stirred resulting in a yellow opaque suspension and is then ready for disperion (Fig. A.4.1d).





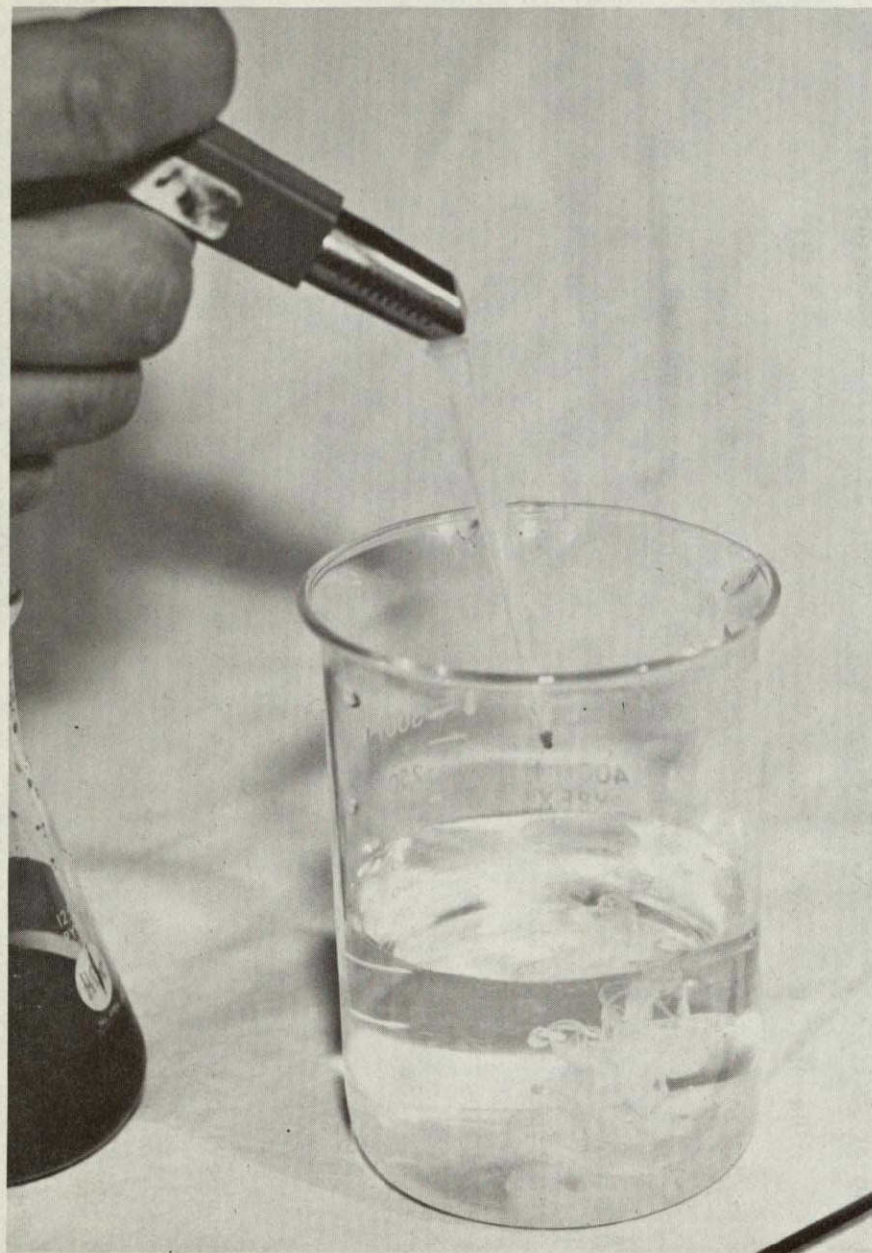
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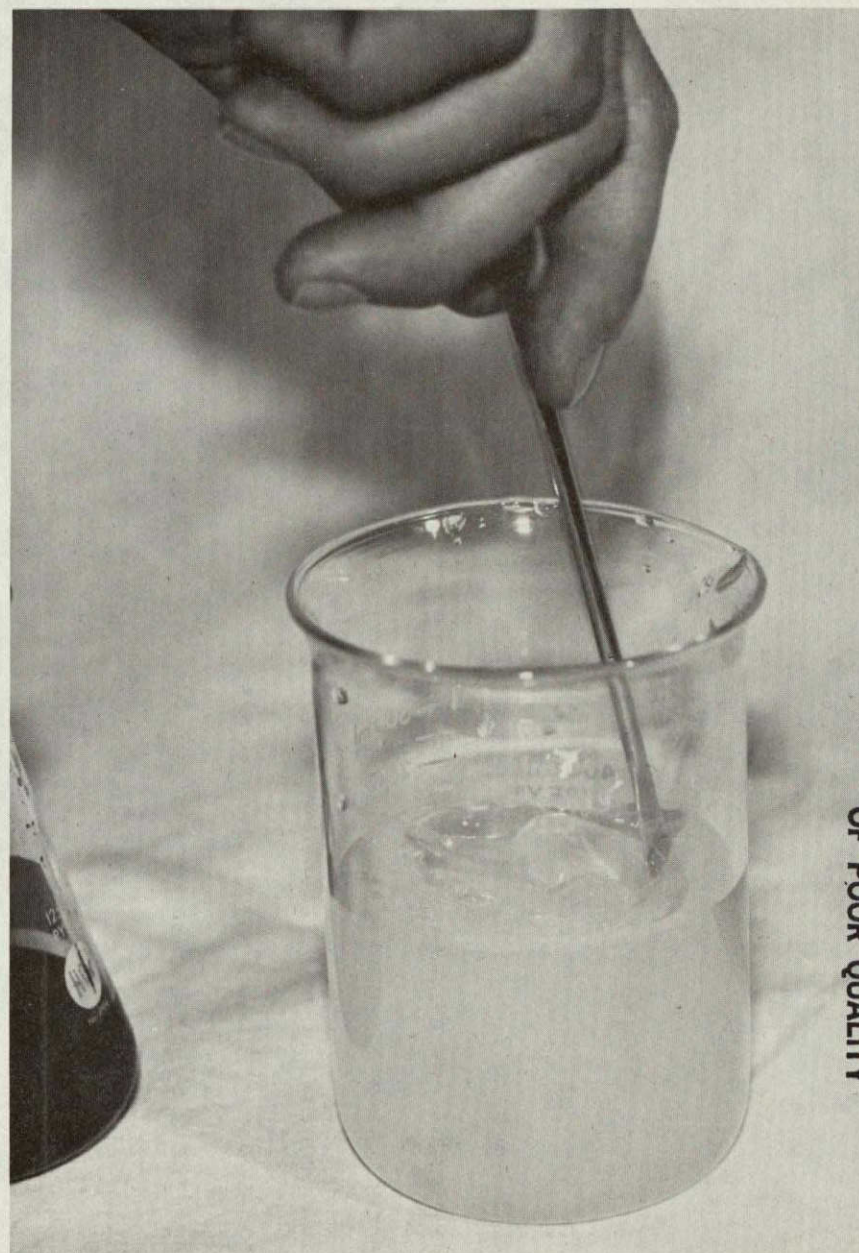
4.A.1b

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4.A.1c



4.A.1d

Figs. 4.A.1a-d: Preparation of AgI suspension.



## 2. Atomization

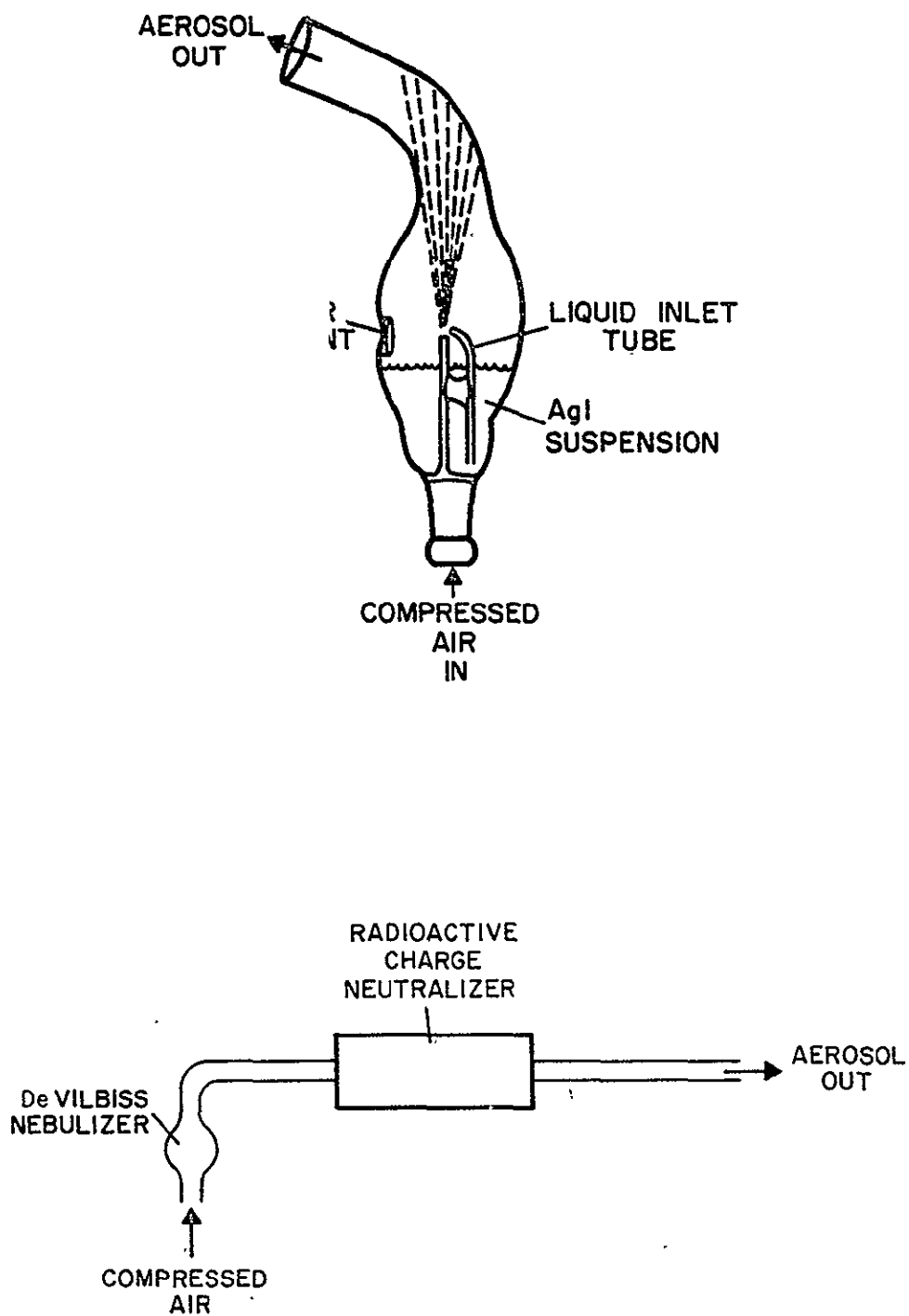
The simplest way to aerosolize a suspension is by breaking the bulk liquid containing the particles into many tiny droplets; i.e. atomization. Ideally, each tiny droplet would contain one particle, however, depending on the concentration of particles and on the size of the droplets, multiplets (droplets containing more than one particle) or droplets containing no particles may occur. Once the suspension is atomized, the droplets evaporate, leaving freely suspended aerosol particles.

Atomization of the AgI suspension does not leave a pure AgI particle. Since the suspension consists of AgI particles suspended in a very dilute solution of  $\text{NH}_4\text{I}$  and water, the resulting AgI particle has some residue of  $\text{NH}_4\text{I}$  when the droplet evaporates.  $\text{NH}_4\text{I}$ , being hygroscopic, enhances the ice nucleating activity of the AgI (Davis, et al. 1975) as well as allowing these particles to be active as CCN (discussed in another section). In addition to the  $\text{NH}_4\text{I}$ , there is some residue left from the distilled water impurities. Particles from droplets containing no AgI will consist of  $\text{NH}_4\text{I}$  and distilled water residue.

Three types of atomizer were tested: a DeVilbiss Nebulizer No. 40, a Constant Output Atomizer and a Collison Nebulizer. Each will be discussed separately in the following sections.

### *a) DeVilbiss Nebulizer*

The DeVilbiss Nebulizer No. 40 is a commercially available low-cost nebulizer (Fig. 4.A.2). Compressed air passes through a tube to a small orifice. The air expands as it passes the mouth of the liquid inlet tube causing a pressure drop at that point thereby drawing liquid up through the tube



### SCHEMATIC OF DeVILBISS NEBULIZER SYSTEM

Fig. 4.A.2: DeVilbiss nebulizer system.



and into the air stream. As the liquid enters the high velocity air stream, it is broken up into tiny droplets. The droplets acquire enough momentum so that 99% of the total droplet mass impacts on the nebulizer walls and is returned to the bulk solution (Corn and Esmen, 1976). The median diameter droplet exiting the nebulizer is around  $4\text{ }\mu\text{m}$  with a geometric standard deviation of about 1.8. A schematic diagram of the system used to generate AgI particles using the DeVilbiss Nebulizer is also shown in Fig. 4.A.2.

About 5 ml of the AgI suspension was poured into the DeVilbiss Nebulizer. Dry filtered compressed air was supplied at 5 lpm for the atomization process. The residue particles were passed through a radioactive charge neutralizer in order to ensure a Boltzman equilibrium charge distribution.

The size distribution was measured with the Wyoming Aerosol System (WAS). A typical size distribution for the output of the DeVilbiss Nebulizer is shown in Fig. 4.A.3. A broad size distribution is obtained with a relatively high concentration of large particles ( $>0.1\text{ }\mu\text{m}$ ) compared to the other nebulizers.

#### *b) Constant Output Atomizer*

The Constant Output Atomizer (COA) was developed by Thermo-Systems, Inc. Fig. 4.A.4 shows a schematic of the atomizer assembly. Dry filtered air is supplied at 35 psi and passes through a 0.343 mm orifice (#80 drill hole) where it forms a high velocity jet. The suspension is pumped into the jet by a syringe pump and is atomized. The larger droplets are impacted on the wall and drawn into a closed reservoir. The rest of the atomized drops

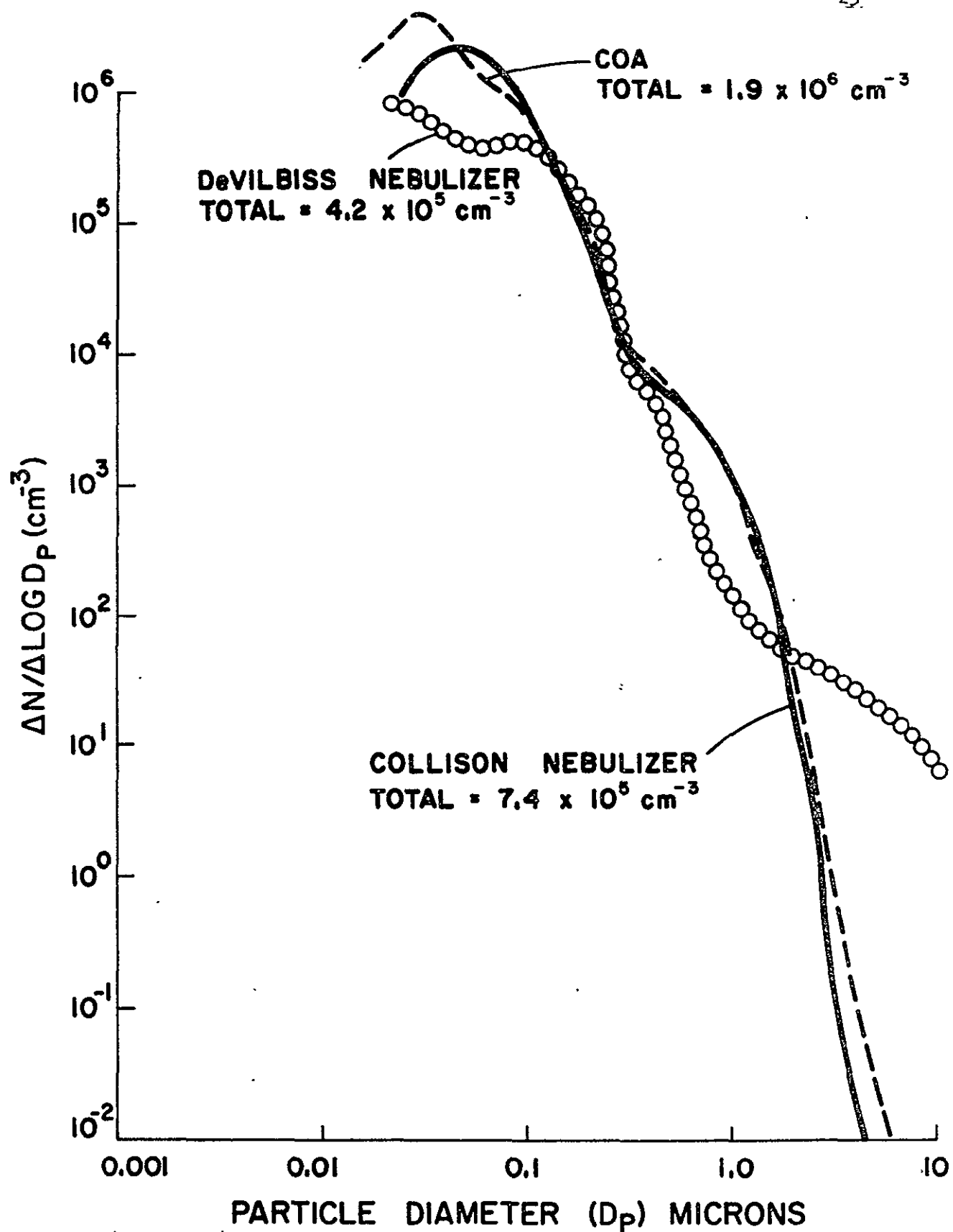


Fig. 4.A.3: Size distributions of dry AgI aerosol nebulized from aqueous suspension.

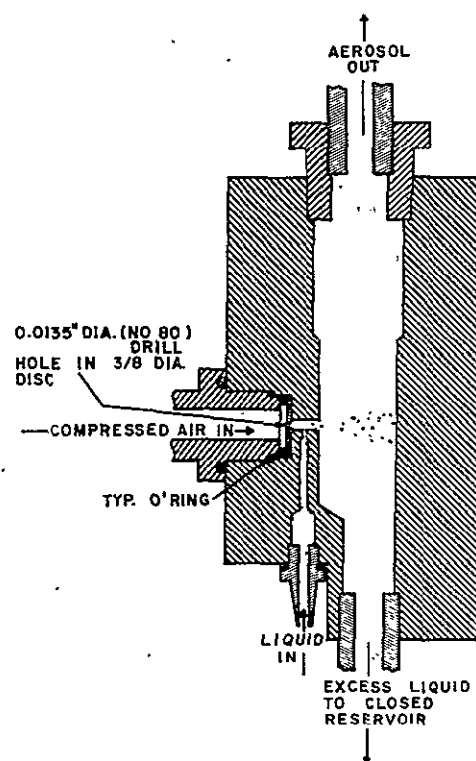
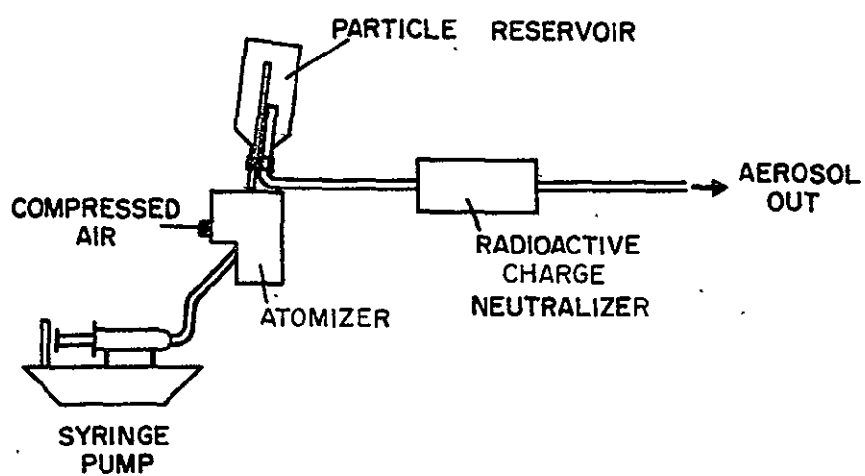


Fig. 4.A.4: Cross section of the constant output atomizer (COA)



**SCHEMATIC OF COA SYSTEM**

Fig. 4.A.5

are carried up and out of the atomizer assembly and into a particle reservoir consisting of a 3 liter glass bottle; this reservoir serves to damp out small scale fluctuations in output. According to the manufacturer's specifications, the median droplet diameter is about  $0.3 \mu\text{m}$ , and the geometric standard deviation is less than 1.9.

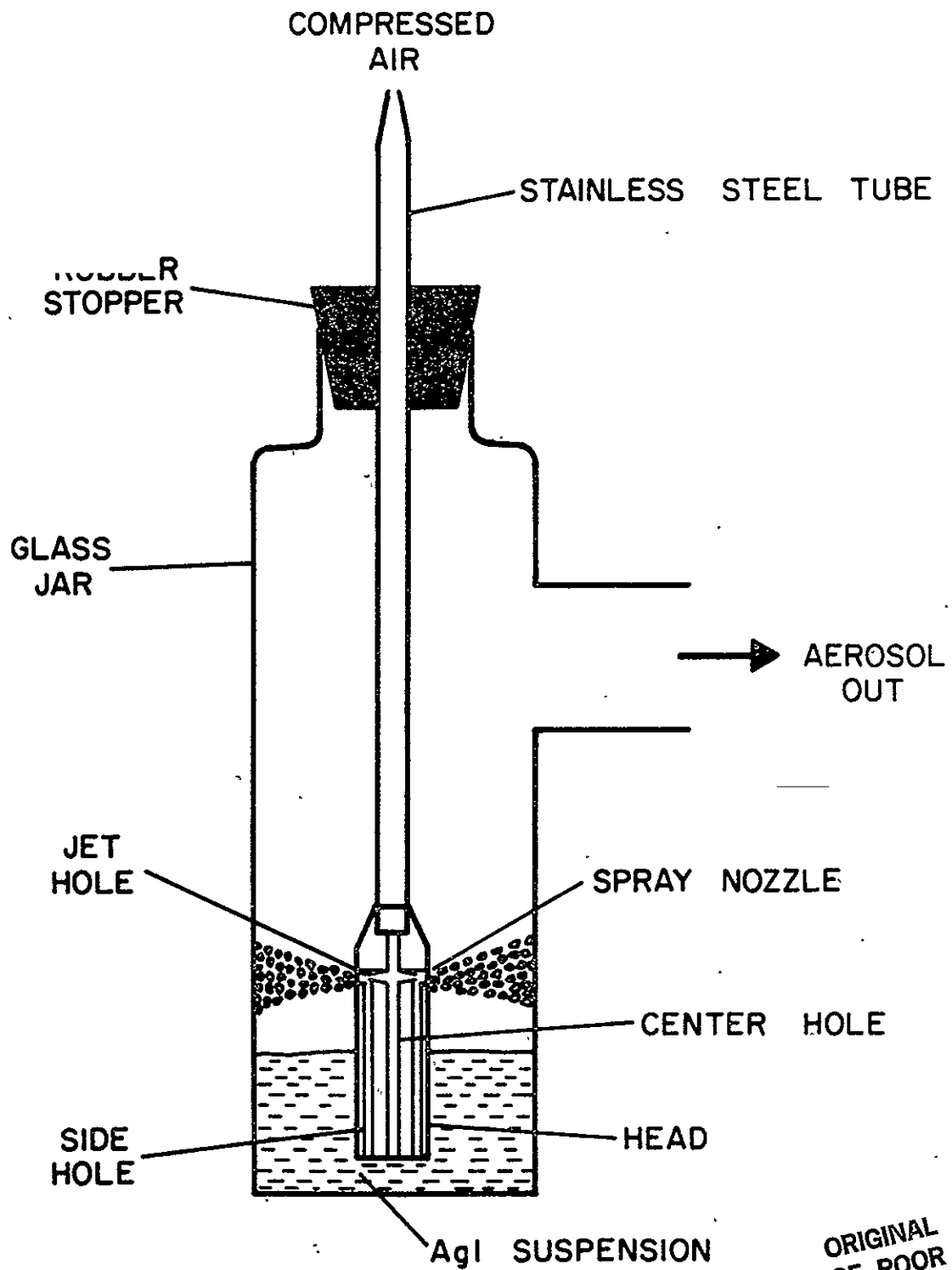
The suspension was aerosolized using the system shown in Fig. 4.A.5. The particles exit the particle reservoir and are neutralized by a radioactive charge neutralizer.

Fig. 4.A.3 shows a typical size spectrum produced by the COA. Because the size distribution of the aerosol is determined by the sizes of the suspended solids, a broad distribution is obtained, very similar to the other methods of atomization. The concentration of large particles ( $> 0.1 \mu\text{m}$ ) is relatively small compared to the concentration of smaller particles due to the order of magnitude decrease in the median droplet diameter produced ( $\bar{d}(\text{COA}) = 0.3 \mu\text{m}$ ;  $\bar{d}(\text{DeVilbiss}) = 4 \mu\text{m}$ ).

This Constant Output Atomizer has been selected for use on the initial ACPL to generate condensation nuclei. Extensive tests have been performed with the device at the Desert Research Institute (Energy and Atmospheric Environment Center) and at General Electric Company (Space Division) to define its characteristics, determine and improve its stability, and adapt it for operation in a low gravity environment.

#### *c) Collison Nebulizer*

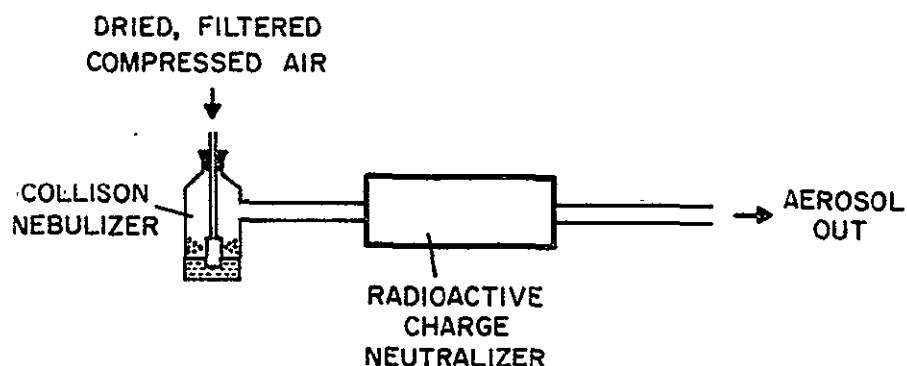
The Collison Nebulizer is widely used to produce solid and liquid aerosols. It is currently available from BGI, Inc., Waltham, Massachusetts for about \$210. A schematic of the nebulizer is shown in Fig. 4.A.6. It consists



**SCHEMATIC OF COLLISON NEBULIZER**

of a stainless steel tube threaded into a stainless steel head. Dry filtered air is fed through the tube and into the head. The bottom of the central hole in the head is closed off so that the air will be forced through a 0.343 mm jet hole and out through a spray nozzle. There are three sets of jet holes and spray nozzles positioned symmetrically around the head. Small side holes run from the bottom of the head up to the point where the air passes between the jet hole and spray nozzle. When the bottom of the head is immersed in a liquid, liquid is drawn up the side hole and into the air jet. The liquid is broken up into drops which exit through the spray nozzles. About 99.92% of the atomized liquid impacts on the walls and returns to the reservoir (May, 1973). Impaction on the walls allows only the smaller droplets ( $< 1.0 \mu\text{m}$ ) to exit the nebulizer (Green and Lane, 1964). Air exiting the spray nozzle along with the droplets carries the droplets out of the jar. A detailed description of the Collison Nebulizer is given by May (1973).

The AgI suspension was aerosolized using the system shown in Fig. 4.A.7. The Collison Nebulizer is fed with 3.0 lpm of air at 12 psig which leaves the



**SCHEMATIC OF  
COLLISON NEBULIZER SYSTEM**

Fig. 4.A.7

nebulizer at 4.4 lpm at ambient pressure. After the aerosol exits the Collision Nebulizer, it passes through a radioactive aerosol neutralizer.

Fig. 4.A.3. shows a typical size distribution produce by the Collision Nebulizer. The spectrum appears to be very similar to that produced by the COA.

### 3. Particle Appearance

A transmission electron microscope was used to examine the AgI particles, since the majority of the particles are below the range of optical microscopes. However, silver iodide exhibits some sensitivity to typical electron beam energies in transmission electron microscopes: silver iodide particles will vaporize under the beam unless they are coated with some heat conducting, less absorbant material, such as carbon. Therefore, the technique for sampling and analysis was more complicated than for other, less sensitive substances.

The suspension particles were aerosolized and collected in a thermal precipitator onto a glass cover slide coated with a thin layer of oil. The cover slide was then vacuum-coated with a thin layer of carbon. Sections of the carbon-coated AgI particles were peeled off the cover slide and floated on distilled water. Finally, electron microscope grids were dipped into the distilled water and pulled out with a small section of carbon-coated AgI particles.

Figure 4.A.8a. and 4.A.8b. show electron micrographs of the AgI aerosol produced from the suspension. Most of the particles are between 0.04 and 0.4  $\mu\text{m}$  in size. Smaller particles which were measured by the aerosol system

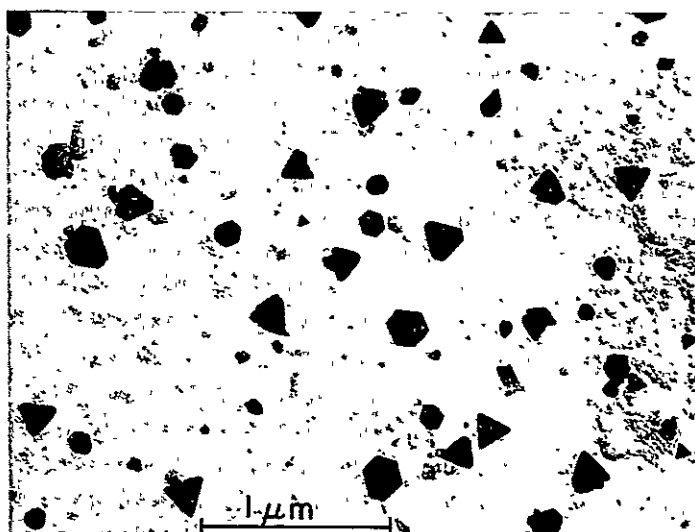


Fig. 4.A.8a

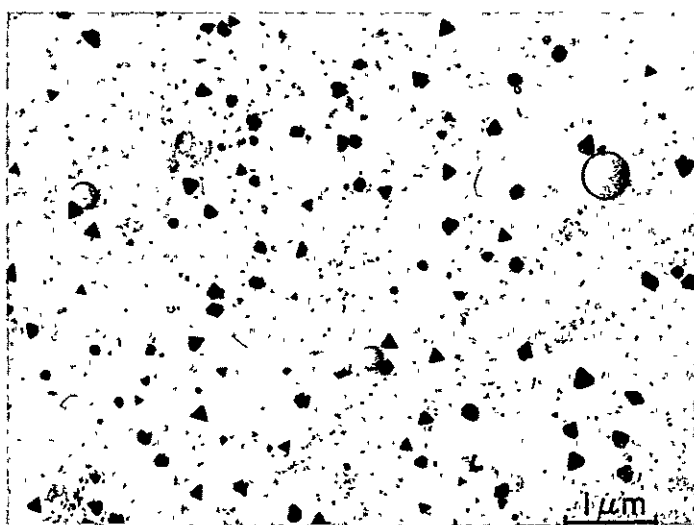


Fig. 4.A.8b

Figs. 4.A.8a and b: Transmission electron micrographs of AgI suspension aerosol.



are not in evidence for two possible reasons: either they are not resolvable from the carbon film substrate or they are composed of droplet residue which did not contain suspended AgI particles, and therefore they may not be stable in the vacuum environment of the microscope. The shapes of the AgI particles are indicative of the hexagonal crystalline structure of silver iodide (alpha). Shadowing with platinum or palladium revealed the three dimensional shapes of the particles to be usually pyramids or truncated pyramids with hexagonal or trigonal bases approximately the same dimension as the height. The photographic evidence of the particles demonstrates the nearly spherical shapes (i.e., not branched or elongated or aggregated, etc.) and also confirms the dominant chemical crystalline composition. Therefore, the particle mass density is probably very nearly equal to that for pure silver iodide (alpha),  $4.33 \text{ g cm}^{-3}$ , and the aerodynamic behavior of the aerosol can be predicted with good confidence.

#### 4. Aerosol Size Classification Experiments

For experiments which include the production of ice crystals in the ACPL cloud chamber using an ice nucleating aerosol, it is desirable to know both the ice nucleating characteristics and the diffusion characteristics of the active nuclei. Nucleation theory (Fletcher, 1969) and experimental results (Garvey, 1973) indicate that nucleation occurs at active sites which are located on the surface of the nucleating material. If the active sites are uniformly distributed across the surface of the material, then the nucleating activity should be proportional to the surface area of the material. Likewise, for particles of homogeneous composition but different sizes, the

the nucleation activity is proportional to the surface area of the particles, and therefore the largest particles should be the most active. These inferences have a direct bearing upon the experimental design, since the diffusion characteristics are also directly related to the particle sizes in a well-known fashion (see for example, Davies, 1966, p. 31ff). Thus, if an experiment required ice particles at rather warm temperatures (above  $-10^{\circ}\text{C}$ ) then the more active, large particles would be used; but the diffusion rates of these particles are substantially slower than for the smaller particles, and this places some time restrictions upon the experiment.

In order to assess the dependence of nucleating ability upon the aerosol size, for the candidate generator output, monodisperse fractions were extracted from the aerosol and tested with the nucleation instruments. The device used for this purpose was the Electrostatic Classifier (EC) Model 3071 made by Thermo Systems, Inc. This device has the ability to produce monodisperse aerosols between the sizes  $0.01\text{ }\mu\text{m}$  for a polydisperse aerosol.

The EC operates on the principle of size sorting on the basis of electrical mobility of singly charged particles. To ensure singly charged particles the aerosol passes through a bi-polar charging unit consisting of a radioactive charge neutralizer which leaves the aerosol with a Boltzman equilibrium charge distribution. Particles smaller than  $0.1\text{ }\mu\text{m}$  from a polydisperse aerosol.

After being electrically neutralized, the aerosol enters the top of the aerosol classifier (Fig. 4.A.9) through an annular sheath. Filtered sheath air flows between the aerosol and the center collecting rod. A

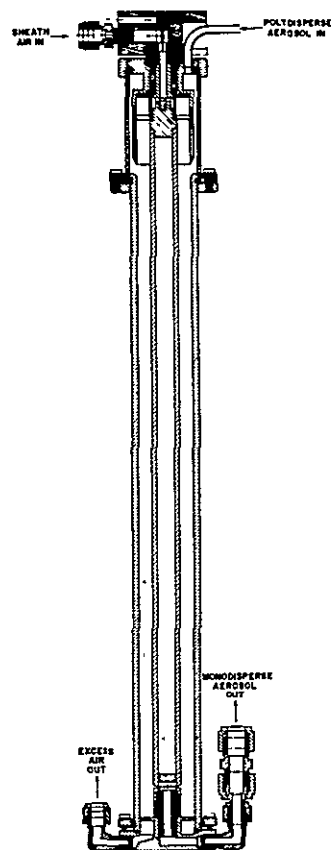


Fig. 4.A.9: Electrical Classifier (EC) from Thermo-Systems, Inc.

negative voltage is applied to the collecting rod causing positively charged particles to move towards the rod. Particles with a high electrical mobility will be collected on the upper portion of the rod while those with lower mobility will be carried along with the excess flow. Only particles having the correct mobility (correct particle size) will be attracted to the exit slit and swept out by a small air stream flowing through the slit. The particle size attracted to the slit is determined by the voltage applied to the collecting rod.

Fig. 4.A.10 shows size distributions measured when the EC is set for unit density spheres of  $0.09\ \mu\text{m}$  and for  $0.2\ \mu\text{m}$  diameter, corresponding to collector

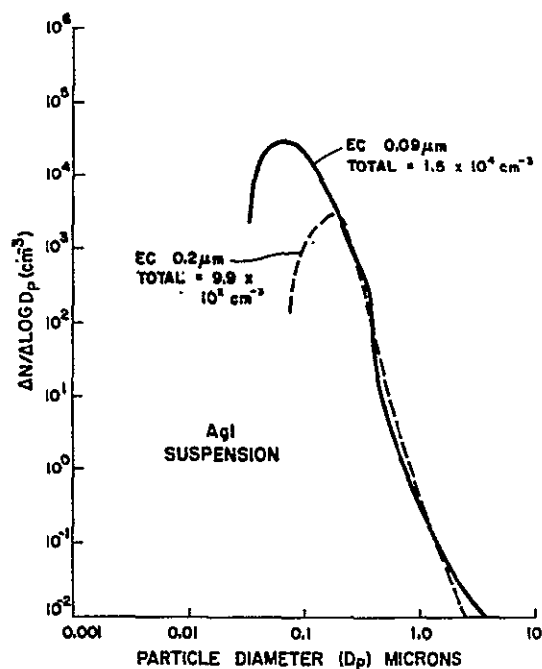


Fig. 4.A.10: Size distributions of the "monodisperse" aerosol.

rod voltages of  $2.7 \times 10^3$  V and  $1 \times 10^4$  V, respectively. The aerosol was generated using the Collision Nebulizer and the AgI suspension; the size spectrum before classification appears in Fig. 4.A.3. The measured distributions are not strictly monodisperse, but a narrow distribution results with the modal particle size corresponding to the setting on the EC. One measure of the monodispersity of an aerosol is the geometric standard deviation,  $\sigma_g$ . A perfectly monodisperse distribution has a  $\sigma_g$  of 1.00. A typical value of  $\sigma_g$  for the AgI suspension in the Collision nebulizer is about 2.1. When this polydisperse aerosol is passed through the EC, the resulting monodisperse aerosol has a  $\sigma_g$  of about 1.6 (as measured with the EAA). The spread of the distributions measured with the WAS is in part due to the "smearing" of size measurements--the exact contribution of this measurement uncertainty is not known. Prior to testing in the nucleation instruments or the aerosol system, the monodisperse aerosol was passed through a radioactive aerosol neutralizer to return the positively charged particles to a Boltzmann equilibrium with zero

net charge. The process of electrostatically classifying the aerosol is not expected to have any effect upon the ice nucleating ability of the silver iodide.

The upper size limit for monodisperse classified aerosol from the EC is  $0.2\text{ }\mu\text{m}$ . Some other means of classifying larger sizes of the AgI aerosol was needed in order to examine the nucleating ability of the larger, more active particles. For this purpose, the EAA was used as a sort of "high pass" filter: The EAA operates by precipitating most of the small particles and measuring the current due to the remaining larger charged particles. We transferred these remaining larger particles out of the EAA via metal tubing located just upstream from the electrometer filter. The sample then passed through a radioactive neutralizer and into a rigid ten liter vessel (because of the vacuum operation). The contents of this vessel were then flushed into a 150 liter aluminized mylar bag and diluted for the nucleation tests. An example of this type of classified aerosol appears in Fig. 4.A.11. The EAA precipitating voltage was adjusted to 7180 volts, such that all charged particles smaller than  $0.26\text{ }\mu\text{m}$  were removed. Notice from the size spectra that the small particles were substantially reduced in concentration; in fact, they were too few to obtain a measurement of the classified aerosol with the EAA. The figure also demonstrates that the larger particles remained in approximately the same concentration in both the unclassified and classified aerosols.

The results of the nucleation tests on the monodisperse, classified and polydisperse aerosols are presented in the next section.

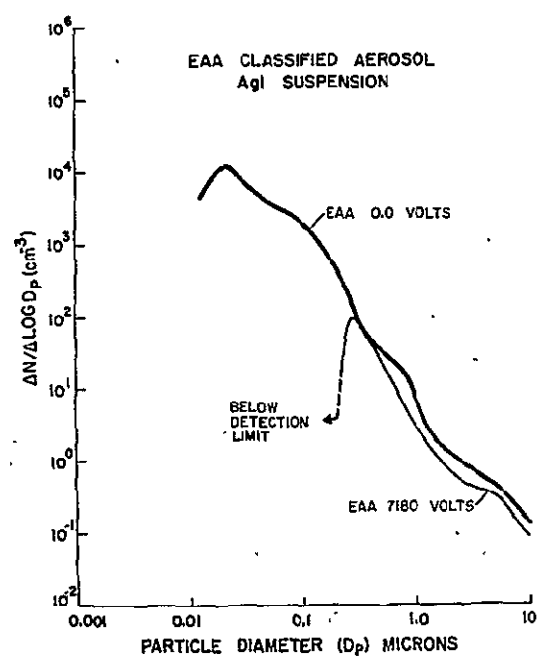


Fig. 4.A.11: Size distributions of aerosol classified with the EAA.

## 5. Ice Nucleus Activity

Due to the complex composition of the suspension particles and the possibility that these particles would nucleate ice through several nucleation processes, several ice nucleus measuring instruments were used to determine the activity of the suspension particles. The instruments used were the DFC, SCC and thermal gradient diffusion chamber.

### *a)*

DFC measurements were made on the AgI suspension at various temperatures using the Collison Nebulizer and the DeVilbiss Nebulizer for atomization. From the Collison Nebulizer the aerosol was passed through an aerosol duct which brought it to the DFC and to the aerosol measuring instruments. The particle concentration was diluted in the duct by a factor of 354 by adding filtered air in order to get a workable concentration at the DFC. In the case with the DeVilbiss Nebulizer, the aerosol was diluted 100 x in an aluminized mylar bag which was then attached directly to the DFC.

Fig. 4.A.12 shows the ice nucleus activity spectra for both nebulizers. The figure shows the number of ice nuclei per liter output from the nebulizers as a function of temperature. It is apparent from the figure that both nebulizers produce approximately the same nucleus concentration where their measurements overlap. This observation is consistent with the expectation that the nucleating ability is predetermined by the nature of the suspension particles and therefore does not depend strongly upon the characteristics of the nebulizer. The figure also indicates that large numbers of ice nuclei can be generated, even for active temperatures as warm as  $-4^{\circ}\text{C}$  (cf., 50 per liter at  $-4^{\circ}\text{C}$ ).

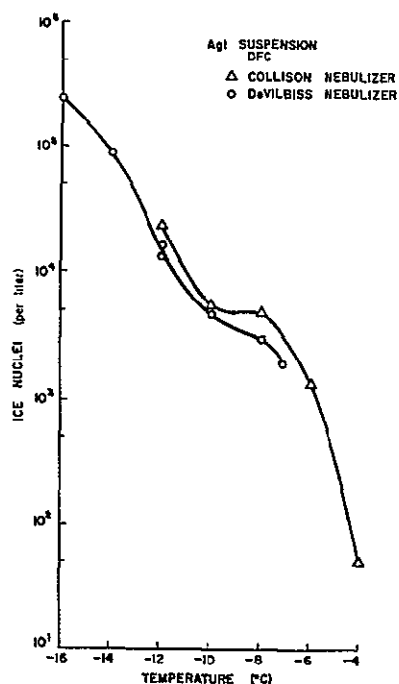


Fig. 4.A.12: Ice nucleus spectrum of the AgI suspension as measured with the DFC instrument.

b)

The results of the nucleation tests for the classified aerosol are given in Fig. 4.A.13. The data points for the EC are plotted at the selected monodisperse size. The total number of EC particles was taken as the cumulative concentration larger than 1/3 of the selected diameter; in this manner the finite width of the classified aerosol and the limited resolution of the EAA measurement were taken into account. The EAA classified aerosol is shown as extending to larger sizes than the selected cutoff, 0.26  $\mu\text{m}$ ; this reflects the actual size distribution (cf. Fig. 4.A.11). There are several important features in Fig. 4.A.13:

1. The most active particles are the largest particles, in agreement with expectations.
2. The increase of active fraction with size parallels a slope of approximately +2; i.e., the active fraction seems to be proportional to particle surface area.



3. Approximately one in a thousand of the largest particles is active at  $-14^{\circ}\text{C}$ ; while this may seem a rather small fraction, it is actually large when compared with other ice nucleating aerosols.
4. The results for the polydisperse aerosol (on the right side of the figure) indicate a smaller active fraction than the large particles of the EAA classified aerosol because of the abundance of small, less active particles.
5. The increase in active fraction with colder temperatures occurs in a roughly uniform manner for the classified and polydisperse aerosols. This increase is approximately a factor of ten to thirty for a cooling of  $6^{\circ}\text{C}$ .

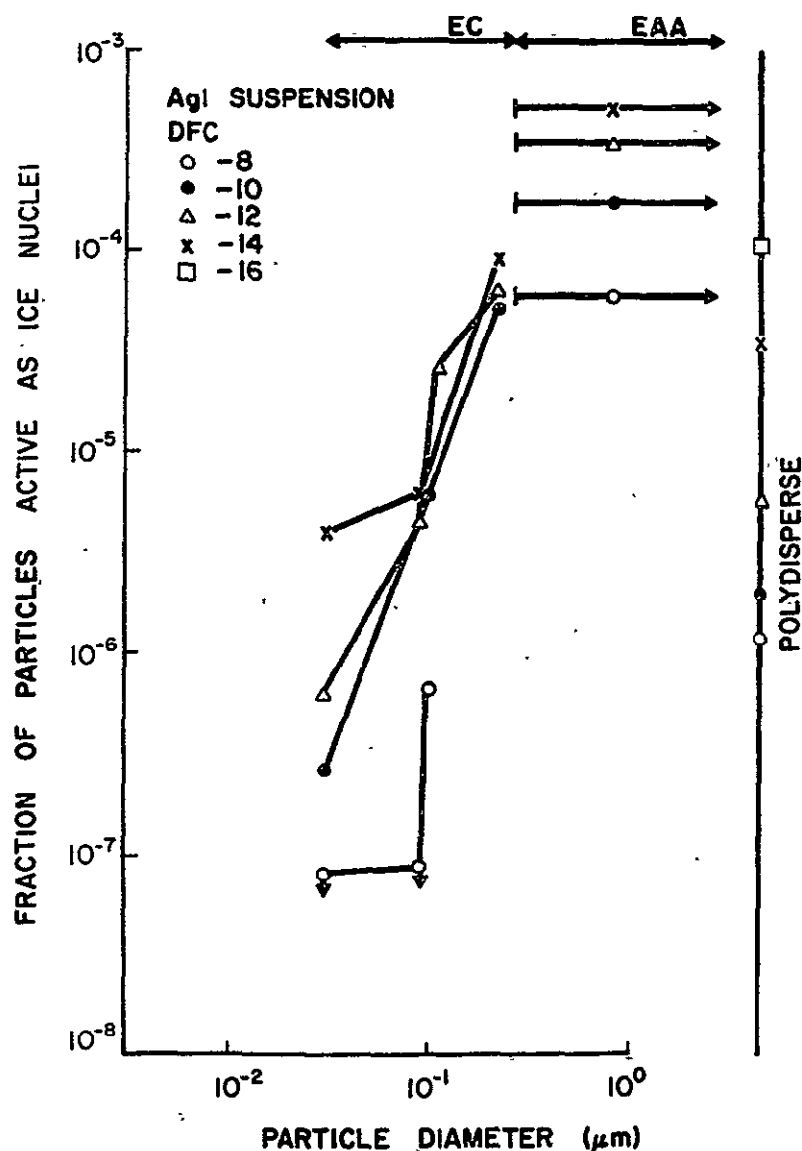


Fig. 4.A.13: Fraction of ice nuclei for classified and polydisperse AgI suspension aerosol.

c)

The immersion-freezing spectra for the AgI suspension were determined using the DFC in a different mode of operation. The suspension was filtered through membrane filters of varying pore sizes; drops of the resulting suspensions were placed on the DFC cold stage and cooled at a rate of  $2.5^{\circ}\text{C min}^{-1}$ . The temperatures at which the drops froze were noted.

The freezing spectra for the filtered suspension and for the unfiltered suspension are shown in Fig. 4.A.14. The curves representing no filter,  $0.8\text{ }\mu\text{m}$  and  $0.5\text{ }\mu\text{m}$  filters indicate that activity at temperatures warmer than

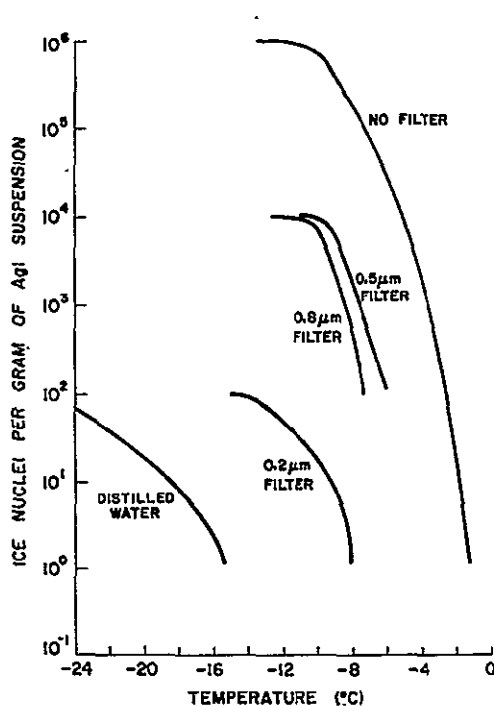


Fig. 4.A.14: Immersion-freezing spectra for the AgI suspension and size-separated subsets.

about  $-6^{\circ}\text{C}$  is due to particles greater than  $0.8\text{ }\mu\text{m}$ . The unfiltered suspension had some activity even at  $-1.5^{\circ}\text{C}$ . Comparing the results obtained using the  $0.2\text{ }\mu\text{m}$  filter with the freezing spectrum for distilled water suggests that there is some activity due to the smaller particles ( $< 0.2\text{ }\mu\text{m}$ ) up to a temperature of  $-8^{\circ}\text{C}$ .

The large range of activity for the unfiltered suspension was measured by making three successive one hundred-fold dilutions of the suspension. The increase in activity with colder temperatures is approximately a factor of  $10^4$  for six degrees cooling in the middle portion of the curve. This increase for the hydrosol is approximately twice as rapid as for the aerosol.

*d)*

The aerosolized AgI suspension for the Collison Nebulizer was collected on membrane filters for processing in the thermal gradient diffusion chamber. Using the EC, size cuts were made and filter samples taken. These filters along with the polydisperse filters were processed at  $-16^{\circ}\text{C}$  and either 12% or 17% ice supersaturation. Results of these tests are shown in Fig. 4.A.15. Again the observations show that most of the activity lies in the large end of the size spectrum.

The response of the AgI activity to increased supersaturation is not very strong with only a factor of about 1.5 increase from 12 to 17%. Results of other research (e.g., Vali, 1976) for thermally generated AgI usually indicate a very strong dependence of AgI activity upon supersaturation, with typical values of increases by a factor of 8 over the same range of supersaturations. The AgI particles generated by evaporation of aqueous suspension have some  $\text{NH}_4\text{I}$  residue or complex on their surface. The deliquescence point

ICE NUCLEUS ACTIVITY OF AgI SUSPENSION  
DETERMINED BY MEMBRANE FILTERS AT  $-16^{\circ}\text{C}$

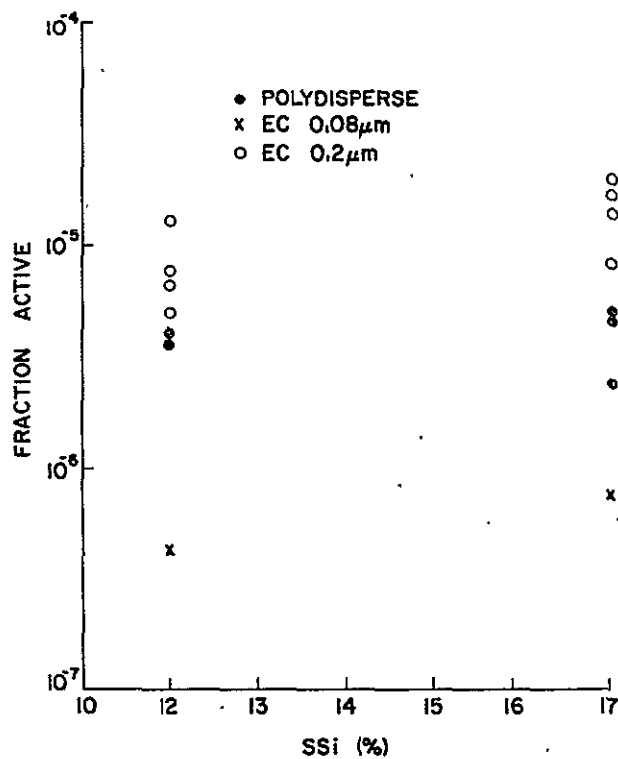


Fig. 4.A.15: Fraction of ice nuclei for classified and polydisperse AgI suspension aerosol (membrane filters).

of  $\text{NH}_4\text{I}$  at  $-16^{\circ}\text{C}$  is about 85% relative humidity with respect to liquid water, or 99% with respect to ice. Since the processor was operated at ice supersaturations of 12 and 17%, liquid water probably condensed upon the aerosol particles, and hence ice crystals formed through an immersion-freezing or condensation-freezing process. This hypothesis would explain the insensitivity of the aerosol to increased supersaturation, since the filter temperature was held constant at  $-16^{\circ}\text{C}$ . The possibility of some nucleation through deposition also exists.



e)

Nucleation tests of the AgI aerosol (nebulized by the Collison Nebulizer) in a cloud chamber (SCC) yielded about 300 ice nuclei per liter at  $-10^{\circ}\text{C}$ . This is about a factor of 10 less than the DFC measurements at  $-10^{\circ}\text{C}$  (Fig. 4.A.12), however, it should be noted that these settling cloud chamber measurements are difficult to make quantitative due to shortcomings in its design. In particular, the coagulation rate of the more active, large particles with cloud droplets is expected to be quite slow compared with the normal experimental times. This problem is less acute in a low gravity environment.

f)

The final test on the activity of the AgI suspension were to determine its stability over a period of time. DFC measurements at  $-10^{\circ}\text{C}$  were made on a freshly prepared batch of AgI suspension aerosolized by the Collison Nebulizer and again 7 and 14 days later. The results, shown in Fig. 4.A.16, indicated that even two weeks after sample preparation the suspension was still capable of producing significant numbers of ice nuclei. This time decay of activity is probably due to several causes: sedimentation of the larger (more active) particles, reduced number concentration of total hydrosol due to coagulation, dissolution of some particles, and reordering of the structure of the particle surfaces. It is well known that a freshly produced AgI surface is usually a more active ice nucleant. The change in aerosol size distribution with time (using the same suspension) is depicted in Fig. 4.A.17. A different type of size distribution plot was used to demonstrate the changes; if these spectra were plotted in the conventional manner (such as Fig. 4.A.11), the plot lines would lie nearly on top of one another and be

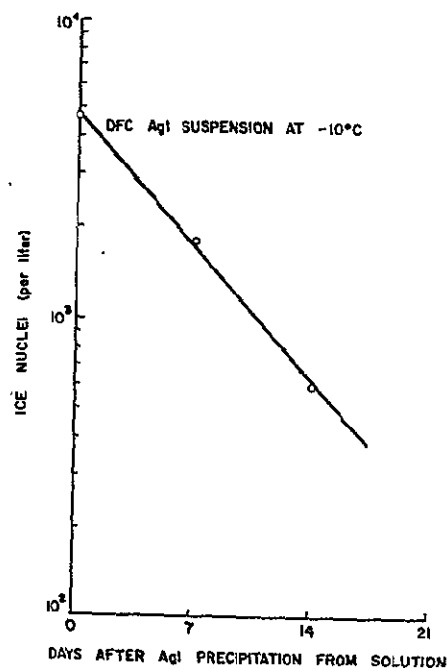


Fig. 4.A.16: Time dependence of AgI suspension activity.

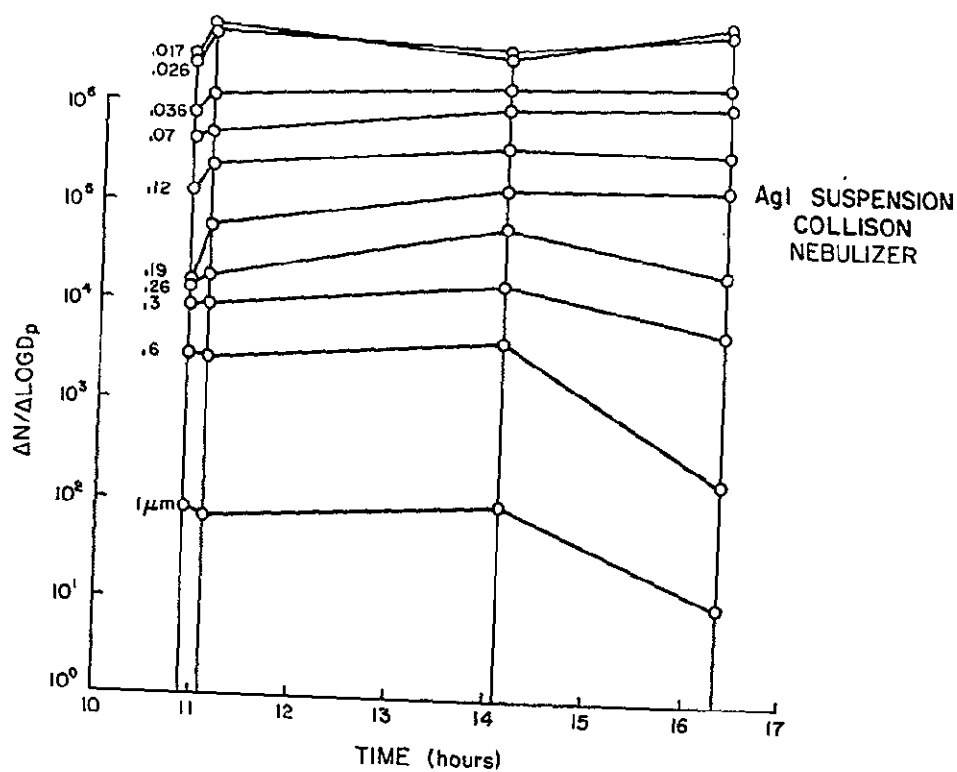
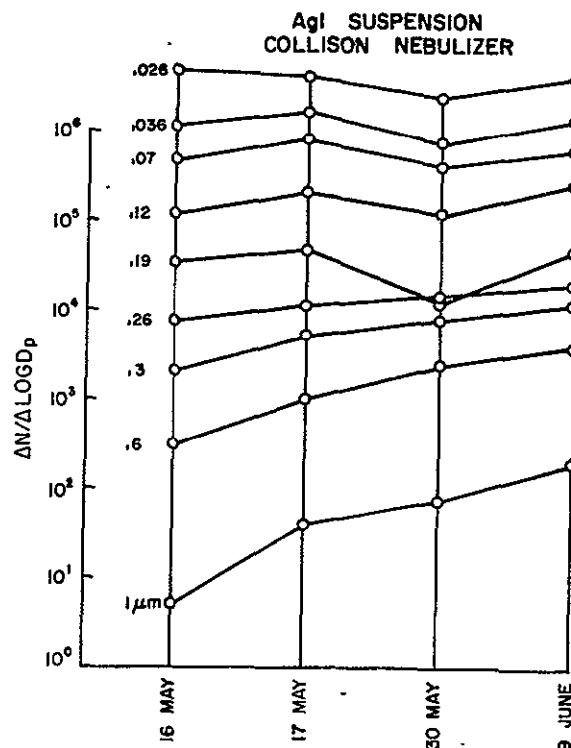


Fig. 4.A.17: Temporal plot of dry aerosol size distributions generated from the same AgI suspension which was precipitated at 1030.

difficult to distinguish. The suspension was precipitated at 1030 and was used to generate aerosol in the Collision nebulizer. The four size spectra of the polydisperse aerosol indicate very little change in concentration for particles of  $0.3 \mu\text{m}$  diameter and smaller. There is an apparent decrease in the larger particles after about 5 hours. The decrease is consistent with the long term decrease in activity and the greater activity of the larger particles.

For all of the nucleation studies in this research, a fresh batch of AgI was precipitated each experimental morning and discarded the following morning. The day-to-day reproducibility of both size distribution and activity was excellent. Fig. 4.A.18 presents four aerosol size spectra generated from independent fresh preparations of the AgI suspension. Particles  $0.3 \mu\text{m}$  in diameter and smaller were generated in nearly equal concentrations. There is an indication of increasing concentration of the larger particles with time; there is no apparent reason for this increase.

Fig. 4.A.18: Size distributions of dry AgI aerosol generated from fresh AgI suspensions.



### B. Evaporation of a Nebulized Solution of AgI-NH<sub>4</sub>I Complex

This technique relies on the fact that silver iodide can be maintained in aqueous solution with a mole ratio of 2.5 to 1 (NH<sub>4</sub>I to AgI). When this solution is atomized, the solvent (water) evaporates and a silver iodide/ammonium iodide complex solid precipitates. These complex aerosols have been shown in earlier work to have good ice nucleating ability (e.g., Davis *et al.*, 1975). The size distribution and concentration of the resulting aerosol depend upon the solution concentration and the characteristics of the nebulizer. For these tests, we used the Constant Output Atomizer (COA, Thermo-Systems, Inc., Model 3075) with a syringe pump metering the liquid flow rate. This atomizer produces droplets which are rather small for an atomization type of device (0.3  $\mu\text{m}$  diameter) with a rather narrow size distribution (geometric standard deviation less than 1.9). With these well defined aerosol sizes, it is a simple matter to generate particles in the primary size range of interest, generally 0.01 to 1  $\mu\text{m}$  diameter. A typical size distribution for this technique is given in Fig. 4.B.1. Notice that particles occur in relatively high concentrations for particles smaller than about 4  $\mu\text{m}$ . The broad size distribution of this aerosol suggests that this aerosol has good versatility for modifying it to prescribed sizes and concentrations.

The particles produced by nebulization of the ammonium-silver iodide solution should act as condensation-freezing nuclei since they are hygroscopic. The nucleation of ice may proceed by two separate processes with this material. Initially the material will pick up water by condensation and will grow as a solution droplet. If the particles experience an environment which is water supersaturated, the droplet will grow to an extent which will cause



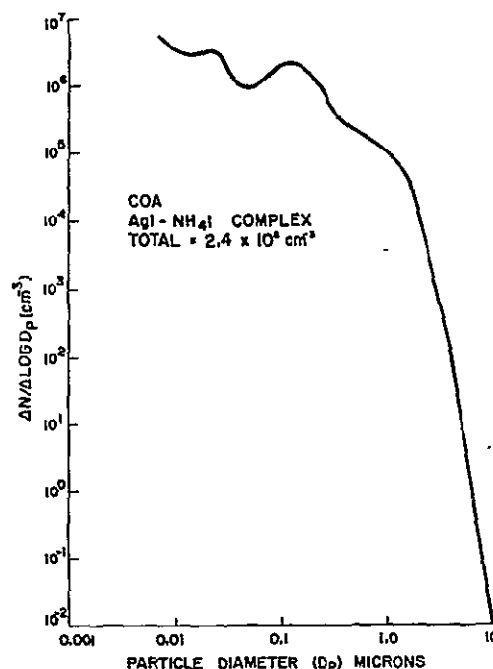


Fig. 4.B.1: Size distribution of dry  $\text{AgI-NH}_4\text{I}$  complex aerosol nebulized from aqueous solution.

the droplet to become dilute enough to precipitate AgI. The freshly precipitated AgI may then act as a freezing nucleus. This mode of nucleation offers the advantage that the AgI is produced in the cloud and presents a fresh surface of nucleant to the droplet. The ice nucleating ability of hydrosols of this type of AgI has been studied by Reischel (1976) and found to be quite good and very reproducible.

If the droplet does not experience a humidity greater than 100% the possibility exists that a complex hydrate ( $3\text{AgI} \cdot \text{NH}_4\text{I} \cdot 6\text{H}_2\text{O}$ ) may crystallize from solution and act as an ice nucleus. Davis *et al.* (1975) have studied the crystal structure of this hydrate and have also found it to be a very active ice nucleant.

Aerosol particles from the ammonium iodide solution generator were examined under the electron microscope. The particles were found to be nearly spherical, as shown in Fig. 4.B.2. Their shape is an advantage from the point of view of predictability of aerosol behavior.

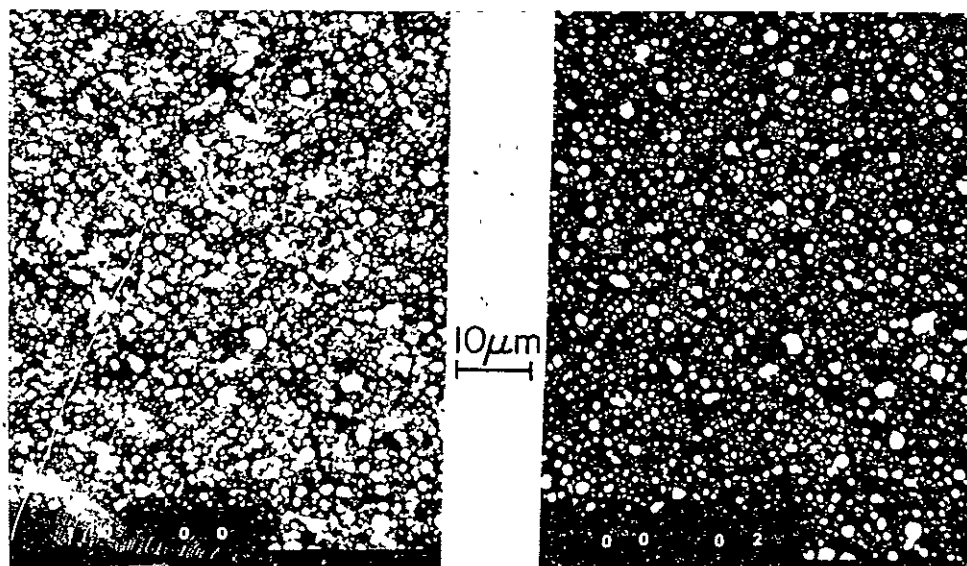


Fig. 4.B.2: Scanning electron micrographs of AgI complex aerosol.

The ice nucleating activity of the aerosol was tested using the settling cloud chamber and also by capturing aerosol on filters for processing in the thermal gradient diffusion chamber. For purposes of these tests, the aerosol was generated in sufficient quantity to fill a 1-m<sup>3</sup> storage bag and samples were drawn from this bag periodically so that repeated measurements could be obtained and the aging characteristic of the aerosol examined at the same time. These tests confirmed the expected good nucleating activity of the aerosol and also showed that the generation of this aerosol in useful concentration can be quite readily accomplished. It is important to note that a significant advantage of this approach is that silver iodide is generated from an aqueous solution at temperatures well below the dissociation point of silver iodide (about 550°C) so that no vapors other than water vapor are produced. Thus no "contaminant" vapors from the generator enter the system. If necessary, the concentration of water vapor can be easily reduced with a diffusion type dryer.

The ice nucleus activity of this aerosol was tested on membrane filters, in a thermal gradient diffusion chamber, and in the cloud chamber. The filter results are shown in Fig. 4.B.3. The fraction of active particles appears to level off at around  $1.5 \times 10^{-4}$  at the high  $SS_i$  ( $> \sim 20\%$ ). Cloud chamber results show that the active fraction is about  $1.6 \times 10^{-5}$  at  $-18.5^\circ\text{C}$ .

A cascade impactor was used to determine which portion of the size spectrum contained most of the activity. Using the cloud chamber the ratio of the number of ice nuclei detected when particles greater than  $4 \mu\text{m}$  are removed to the number detected when no particles are removed was determined to be typically 0.2. This indicates that about 80% of the active particles are larger than  $4 \mu\text{m}$ . The CCN activity of this aerosol was measured during the Reno Workshop with the continuous flow chambers. Table 4.B.1 summarizes the results of these measurements. Notice that apparently all of the generator particles are active as CCN at fairly low supersaturations. This result is consistent with our expectation of the hygroscopic nature of the silver iodide complex.

TABLE 4.B.1 CCN Activity of Silver Iodide Complex Solution Aerosol.

<u>supersaturation (%)</u>	<u>droplet concentration (<math>\text{cm}^{-3}</math>)</u>
0.18	1312
0.61	2038
1.00	2200
1.95	2354
Aitken counter	$\sim 2300$

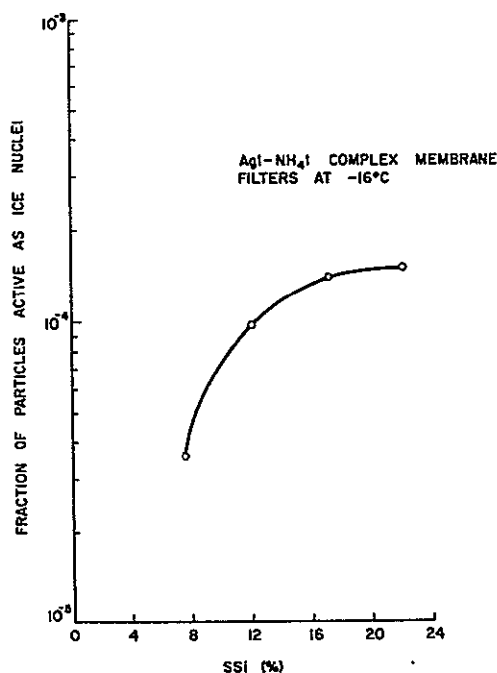


Fig. 4.B.3: Fraction of ice nuclei for AgI-NH<sub>4</sub>I complex aerosol.

There are some operational difficulties with this system. The solution is highly concentrated (approximately 55% solute by weight), so that filtering of the solution ahead of the atomizer is essential. This operation requires the use of a pumping and metering device to overcome the pressure difference and varying flow as the filter becomes clogged. A syringe pump (Howard Apparatus Compact Infusion Pump) was used during these experiments, but its output has been shown to vary slightly, and it is rather heavy, considering the task it is to perform. To overcome these shortcomings, two alternative pumping techniques were investigated. The first method used a high torque digital stepping motor to turn a threaded rod and push a syringe plunger. The motor is driven by a square wave of selectable frequency. This technique was also used for the vibrating orifice generator, and it performed satisfactorily. The other method used regulated gas pressure from a nitrogen storage tank to push the syringe plunger. This pressure

method was found unacceptable because of the increase in filtering pressure which was needed as the filter became clogged. (It performed satisfactorily for the preliminary tests using dilute NaCl solutions, but was not useful for the high concentrations of the silver iodide complex.)

Another operational difficulty of this technique is that, due to the high solute concentrations, the atomizer tended to become clogged after several hours' use, necessitating cleaning with a concentrated solution of ammonium iodide.

#### C. Condensation of AgI vapors within a heated quartz tube

Pure silver iodide substance begins to dissociate at about  $550^{\circ}\text{C}$  and produces sufficient vapors that particles recondense from the vapor at about  $700^{\circ}\text{C}$ . The "hot tube" generator used for evaluation consisted of a quartz tube with a small AgI ampule attached to the side of one end and which was wrapped with several coils of nichrome wire for heating the tube (see Fig. 4.C.1). Variable voltage power supplies provided power for heating the wires. The first coil heats the AgI sample to a temperature slightly above  $700^{\circ}\text{C}$ , producing primary particles and excess vapor. These particles and gases are transported in the carrier gas (clean, dry nitrogen) to the reheating portions of the generator. There the temperature of the gas/particle mixture can be adjusted from below 700 to over  $900^{\circ}\text{C}$ . Thus the particles can be evaporated and recondensed in each of the reheat sections. The evaporation and recondensation cycle is a characteristic feature of LeMer type generators; they have been used with good success to produce monodisperse aerosols of a very wide variety of materials. The temperature at each



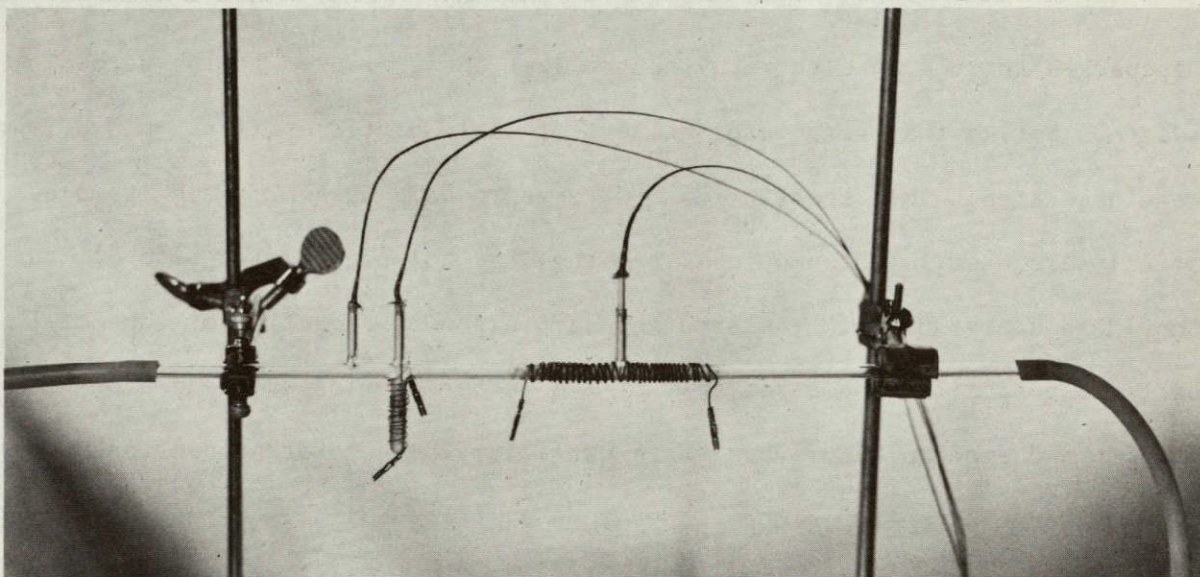


Fig. 4.C.1': Hot tube generator.

of the control points in the generator was measured with alumel-chromel thermocouples, so that experimental conditions were well defined. A typical size spectrum of the product aerosol is given in Fig. 4.C.2; the output

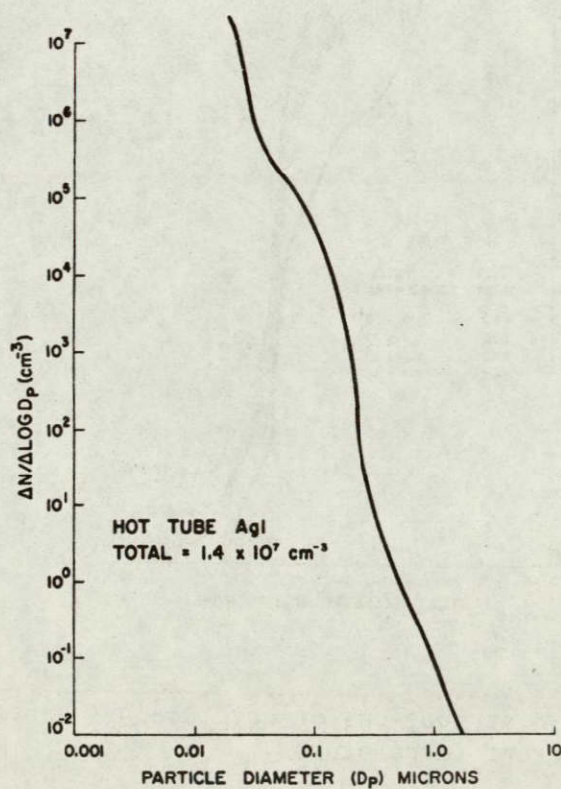


Fig. 4.C.2: Size distribution of hot tube AgI aerosol.



was passed through an electrical neutralizer and a diluter to the aerosol system. Notice that very large numbers of small particles (less than  $0.1 \mu\text{m}$ ) were generated. This spectrum was quite reproducible when "fresh" samples of AgI were used in the ampule (i.e., they had not been heated before), but continued operation with the same AgI sample showed reduction of the total particle production and especially of the larger particles. Generator production and especially of the larger particles. Generator production was also quite dependent upon the temperature of the ampule (as expected); Fig. 4.C.3 shows several different spectra at different temperatures (power supply voltages). Notice that the hotter temperatures (higher voltages) in general produced larger particles and higher concentrations.

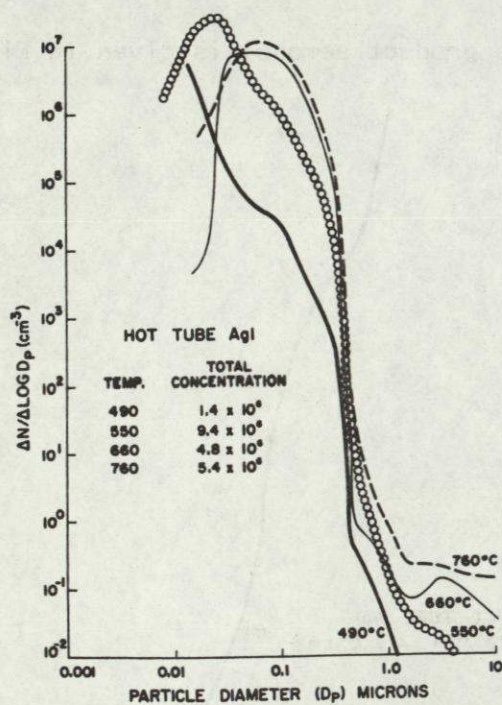


Fig. 4.C.3: Size distributions of hot tube AgI aerosol at four different temperatures.



The transmission electron micrograph in Fig. 4.C.4 shows particles which were produced with the hot tube generator. In general, the particles were spherical in shape, although considerable variations were observed. The hexagonal crystalline structure of silver iodide ( $\alpha$ ) is not obvious in these micrographs; the shapes are more suggestive of an amorphous than crystalline structure.

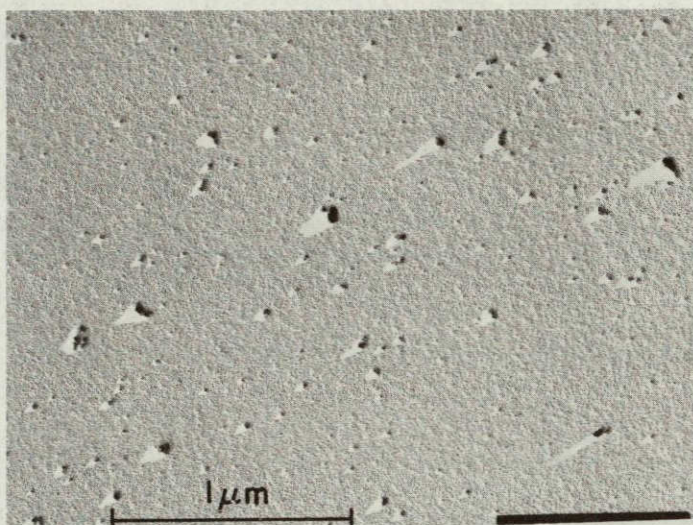


Fig. 4.C.4: Transmission electron micrograph of hot tube AgI aerosol.

The ice nucleating abilities of this aerosol were tested with the settling cloud chamber at two temperatures,  $-15$  and  $-18^{\circ}\text{C}$ . The results from tests at these two temperatures were not significantly distinguishable due to the large variability at one temperature. The generator produced about 20,000 per liter active nuclei at  $-15^{\circ}\text{C}$ . While this concentration seems quite large, the fraction of total particles which were active as ice nuclei



was actually quite small, approximately  $5 \times 10^{-6}$ . This active fraction is substantially smaller than for the nebulized aerosols at the same temperature, and it indicates that the aerosol has a rather low intrinsic activity. No CCN activity measurements were made.

This generating technique was abandoned for use in the ACPL for the reasons enumerated below:

- 1) low intrinsic ice nucleating activity--this means that a very large number of inactive particles would contaminate experiments;
- 2) undesirable byproducts of the generation process, specifically, iodine gas and heat would have to be removed;
- 3) power requirements to operate the heating wires are quite large compared to other generators; this generator required approximately 40 watts.

#### D. Hot Wire Generators

Two different hot wire type generators were studied for silver iodide aerosol generation. The first was a rather simple device, a coil of nichrome wire inside a glass tube. A small amount of silver iodide paste was daubed onto the wire, and the wire was heated to a dull red color (about  $900^{\circ}\text{C}$ ) while dry filtered nitrogen was ventilating the wire inside the tube. The resulting aerosol condensed in the cooler downstream portions of the tube and had to be transferred to a storage container and rapidly diluted to reduce coagulation and diffusion losses. This device and a typical spectrum (corrected for dilution) are shown in Fig. 4.D.1 and Fig. 4.D.2. Notice that the total particle count is very high ( $1.3 \times 10^7 \text{ cm}^{-3}$ ) and that the



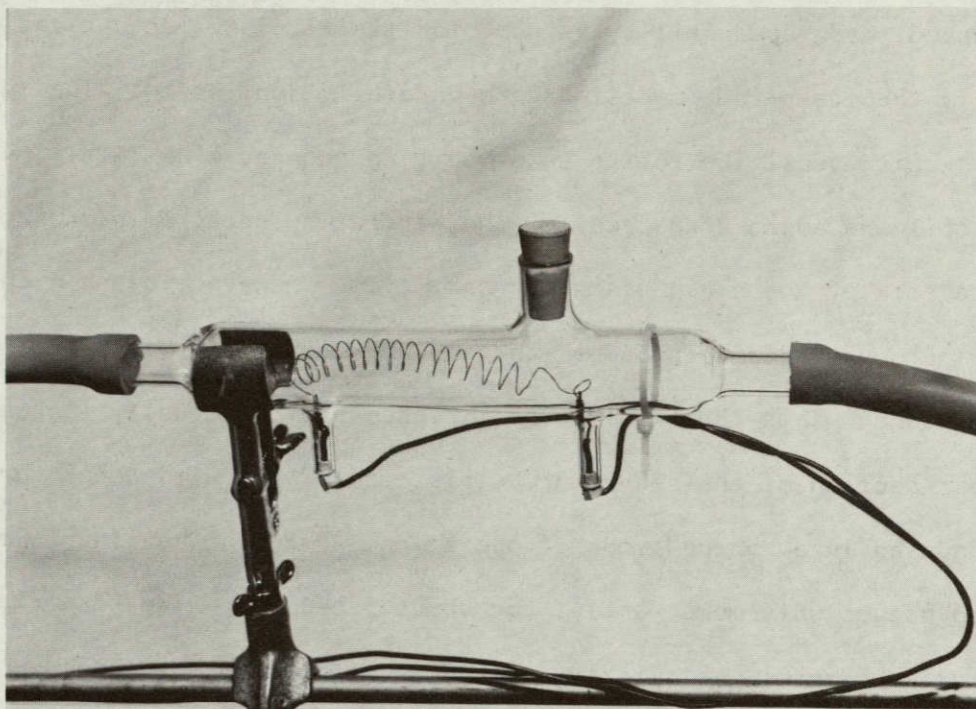


Fig. 4.D.1: Hot wire generator.

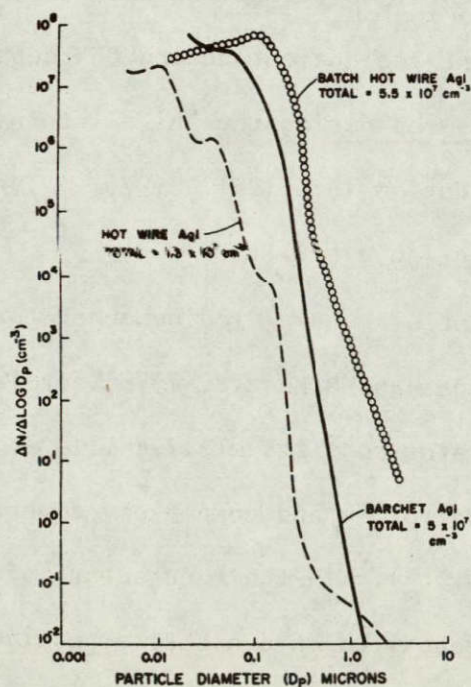


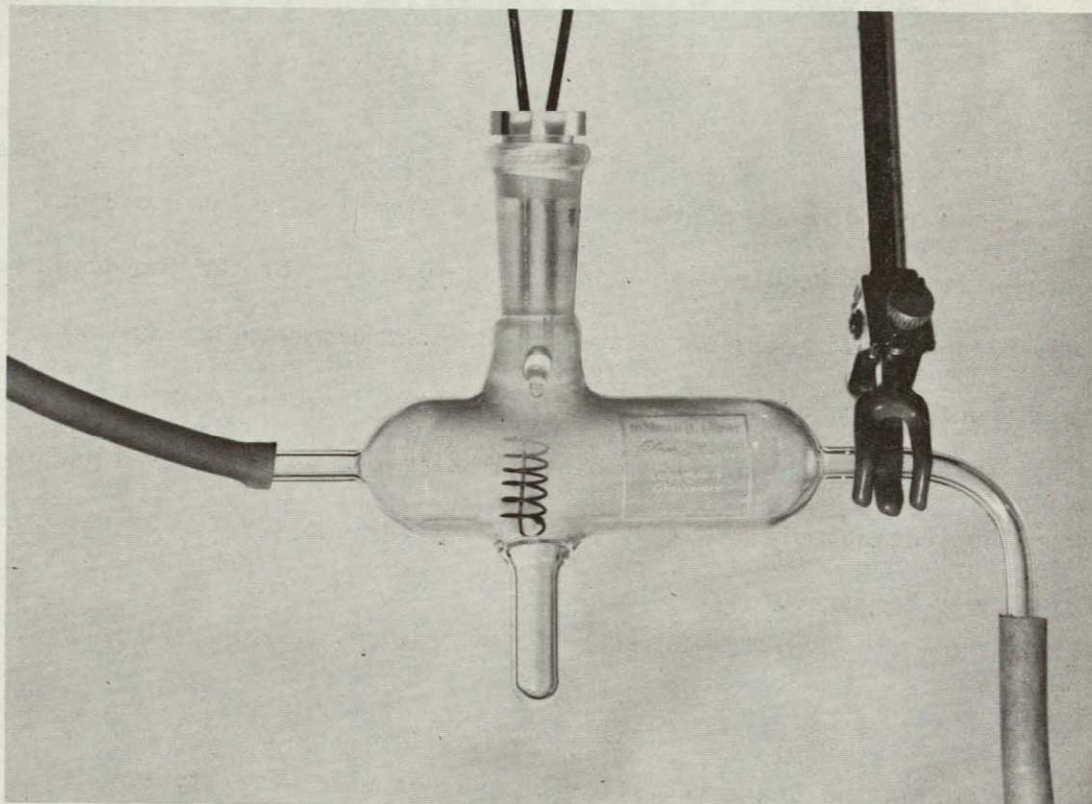
Fig. 4.D.2: Size distributions of hot wire aerosol from three different generators.



modal diameter is rather small, about  $0.02\ \mu\text{m}$ . This aerosol is quite easily produced, and repeatability is good for the size and ice nucleating spectra if the operating conditions are carefully duplicated. The generator output is quite sensitive to the power setting and gas flow rate. A second heating coil was added downstream of the generating section in order to evaporate some of the copious smaller particles. However, clean nichrome wire will produce an abundance of ions and very small particles when heated to about  $900^{\circ}\text{C}$ . Thus the total aerosol concentration actually increased in the reheat section of the generator. This type of hot wire generator has also been used in a "batch" mode of operation, where the heating is more intense and occurs only momentarily, for about 5 seconds. The resulting high concentration aerosol was quickly diluted and stored for prolonged use. A typical aerosol size spectrum for this batch mode before any dilution is also shown in Fig. 4.D.2. The higher supersaturations present during rapid heating produce both a greater concentration and greater size than the cooler, steady operation mode. The ice nucleating and CCN behavior of this aerosol have been fairly well measured during the Third International Ice Nucleus Workshop held in Laramie during 1975 (Vali, 1976). Typical results for this batch aerosol are given in Table 4.D.1.

The second type of hot wire silver iodide generator was developed by Dr. Richard Barchet (Barchet and McKenzie, 1975) for laboratory ice nucleation studies. This generator consists of a ventilated glass tube containing a heating wire which is uniformly and completely covered with a layer of silver iodide (see Fig. 4.D.3). In the manufacture of this wire, a silver plating is electrically deposited on a nichrome heating wire. The silver





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Fig. 4.D.3: Barchet AgI hot wire generator.

plate is then reacted with an excess of iodine gas in a heated environment. The result is a uniform, complete coating of silver iodide on the wire. The generator is operated continuously at temperatures somewhat below the other hot wire device. The aerosol output from this generator is quite reproducible, although the long term output slowly decreases. A typical size spectrum for the steadily operating Barchet generator is given in Fig. 4.D.2. Notice that the output is quite similar to the other hot wire generators. The concentration of small particles is very large, and coagulation occurs rapidly so that the samples must be significantly diluted (by factors of 100 to 1000) for measurement and nucleation tests. A summary of the nucleation characteristics of this aerosol is also given in Table 4.D.1. Notice that the active fraction ( $10^{-6}$  to  $10^{-7}$ ) is substantially less than the nebulized suspension aerosols which were described in a previous section.



These two hot wire generators were quite simple to use and did not have excessive power requirements (less than 40 watts for the two stage hot wire device and less than 7 watts for the Barchet generator). However, they did fall short of the criteria for use in the ACPL. Their worst shortcomings were the production of contaminants (iodine gas and heat) and the lack of strong nucleating ability (they had low intrinsic activity and rather cold threshold temperatures).

Table 4.D.1

Ice Nucleating Characteristics of the Hot Wire Generators.

(The values are calculated to omit all dilution factors.)

	<u>Filter Measurements</u>			<u>Settling Cloud Chamber</u>	
	$\alpha$ (per liter)	$\gamma$	Active fraction at $-16^{\circ}\text{C}$ W.S.	Concentration (per liter)	Active fraction
hot wire (batch operation)	$3 \times 10^4$	7.3	$2 \times 10^{-6}$	$\sim 10^7$	$\sim 10^{-3}$ @ $-12^{\circ}\text{C}$ (Ohtake Chamber)
Barchet	$2 \times 10^4$	3.5	$4 \times 10^{-7}$	$10^3$	$2 \times 10^{-7}$ @ $-15^{\circ}\text{C}$ (Wyoming Chamber)

#### E. Vibrating Orifice Monodisperse Aerosol Generator

The principles of operation of this device have been well known for about one hundred years. A cylindrical jet of liquid is formed as the liquid is pumped through a small orifice. Instabilities which form on this liquid stream will cause it to break up into sausage-like pieces which collapse



into droplets some distance downstream from the orifice. The size of the droplets can be controlled to some extent by vibrating the orifice such that all of the sausage-like pieces are of the same length (which is determined by the frequency of vibration). In the case of our experiments, we used a RNB Associates, Inc., Model 50A which we termed the Berglund-Liu (B-L) generator, after the developers. We tried using a saturated solution of silver iodide in distilled, deionized water, where we counted on the low solubility of silver iodide in water (about  $10^{-7}$  grams per ml) to provide a low concentration. The droplets produced by the generator evaporated to leave the solute residue, whose size was dictated by the initial solute concentration and the droplet volume. A typical size spectrum of this aerosol appears in Fig. 4.E.1. The spectrum was not measured below  $0.1 \mu\text{m}$  since the overall concentration ( $350 \text{ cm}^{-3}$ ) was too small for the Electrical Analyzer to accurately measure; i.e., it is near the threshold concentration for this device. Notice that the spectrum is indeed of monodisperse shape and the modal diameter is of the expected size. A sample of these particles for the electron microscope (Fig. 4.E.2) revealed that they were nearly spherical and amorphous. The particles were found to be sensitive to vacuum and to electron bombardment (they seemed to evaporate in the electron beam). The impurity levels in the distilled, deionized water are comparable with the solubility of silver iodide, so that the aerosol particles which form would be some complex or mixture of silver iodide and impurities. Their ice nucleating properties were not very encouraging, with only 0.5 nuclei per liter at  $-16^\circ\text{C}$  and water saturation in the filter processor; this corresponds to an active fraction of  $1.5 \times 10^{-6}$ . Because of the limitations of impurity



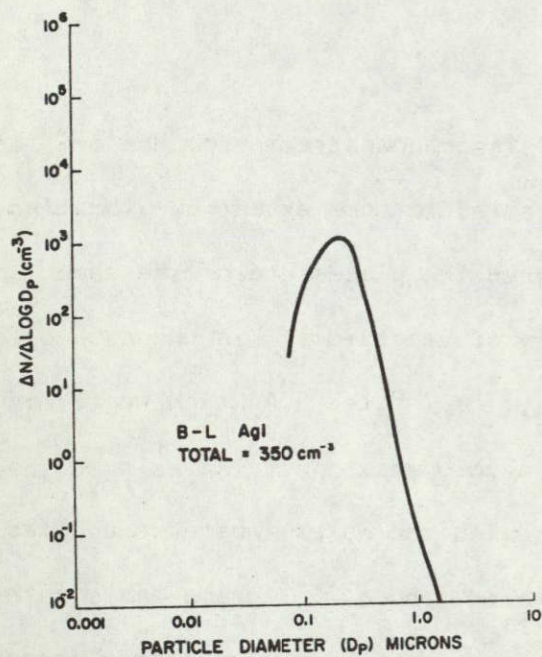


Fig. 4.E.1: Size distribution of dry AgI aerosol from vibrating orifice generator.

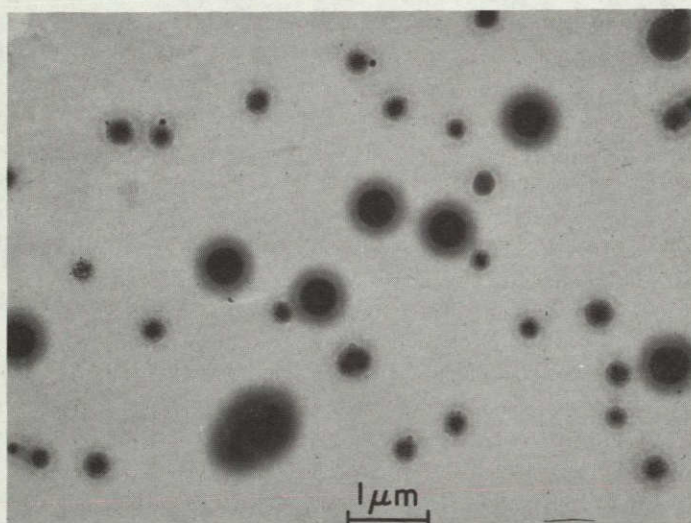


Fig. 4.E.2: Transmission electron micrograph of AgI aerosol from vibrating orifice generator.



concentrations and the smallest monodisperse droplet,  $0.4\text{ }\mu\text{m}$  is about the smallest particle that can be produced with this generator.

An alternative liquid solution for this generator uses a solubilizing agent (ammonium iodide, for instance) to increase the solubility of the silver iodide. However, the solute concentration has to be quite large for the silver iodide to remain in solution. The small orifices ( $10$  and  $20\text{ }\mu\text{m}$ ) have had clogging problems with much less concentrated solutions, and trying to use a highly concentrated solution makes the problem worse. The other problem with this type of generator is that it often requires a considerable amount of the operator's attention to get it started and to keep it going. Finally, the range of aerosol sizes which could be produced is too restricted.

#### V. SUGGESTIONS FOR AN ICE NUCLEUS GENERATOR FOR THE ACPL

As the preceding portions of this report indicated, the aqueous suspension of AgI is our best recommended ice nucleating material, and the most appropriate generating method is atomization. The performance characteristics of the three nebulizers are quite similar, although we preferred to work with the glass Collison because of its simple, compact design and the ease with which it is cleaned. The device could not be operated in zero gravity in its usual configuration because the impacted large droplets would not experience a force to return them to the liquid reservoir, but there are several alternative ways to circumvent this problem.

The first alternative consists of impacting the droplets onto a porous, permeable surface (such as sintered brass) and removing the liquid by suction. The liquid would then have to be discarded since it is anticipated

that a substantial fraction of the suspended particles would not be transmitted through the permeable substance, and therefore, the size distribution of the aerosol would change with time if the liquid were recirculated. This mode of operation would be rather inefficient, since the liquid throughput rate of the nebulizer is large compared to its aerosolized output. The nebulizer sprays about 5 ml of liquid per second, and of this amount only about 0.2% (0.01 ml per second) is actually aerosolized. In the case where only a small batch of ice nucleating aerosol were required, this method would probably suffice; but in general, a substantial amount of liquid would accumulate for discarding (e.g., 3 liters in 10 minutes).

In the second alternative the droplets would be impacted on the liquid surface of the suspension, and the suspension would recirculate through a liquid-gas separator to the liquid feed inlet. Unfortunately, there are several problems with this system. The liquid feed rate and the recirculating rate would have to be carefully matched to avoid the accumulation of liquid anywhere in the circuit. Furthermore, the liquid-gas separator must not affect the hydrosol concentration or size distribution.

Both of these aforementioned problems are avoided in the third alternative in which centripetal force is used to confine the liquid in a reservoir where the liquid itself provides in a non-interfering impaction surface for the large drops. Fig. 4.A.1 shows the fundamental components of this system. The liquid is rotated inside a cylindrical chamber by a chemically inert magnetic stirring bar. The centripetal force would separate the liquid from bubbles which form where the nebulized jet impacts on the liquid. Thus the liquid feed tube would not draw in air bubbles, and its stable operation would be assured.

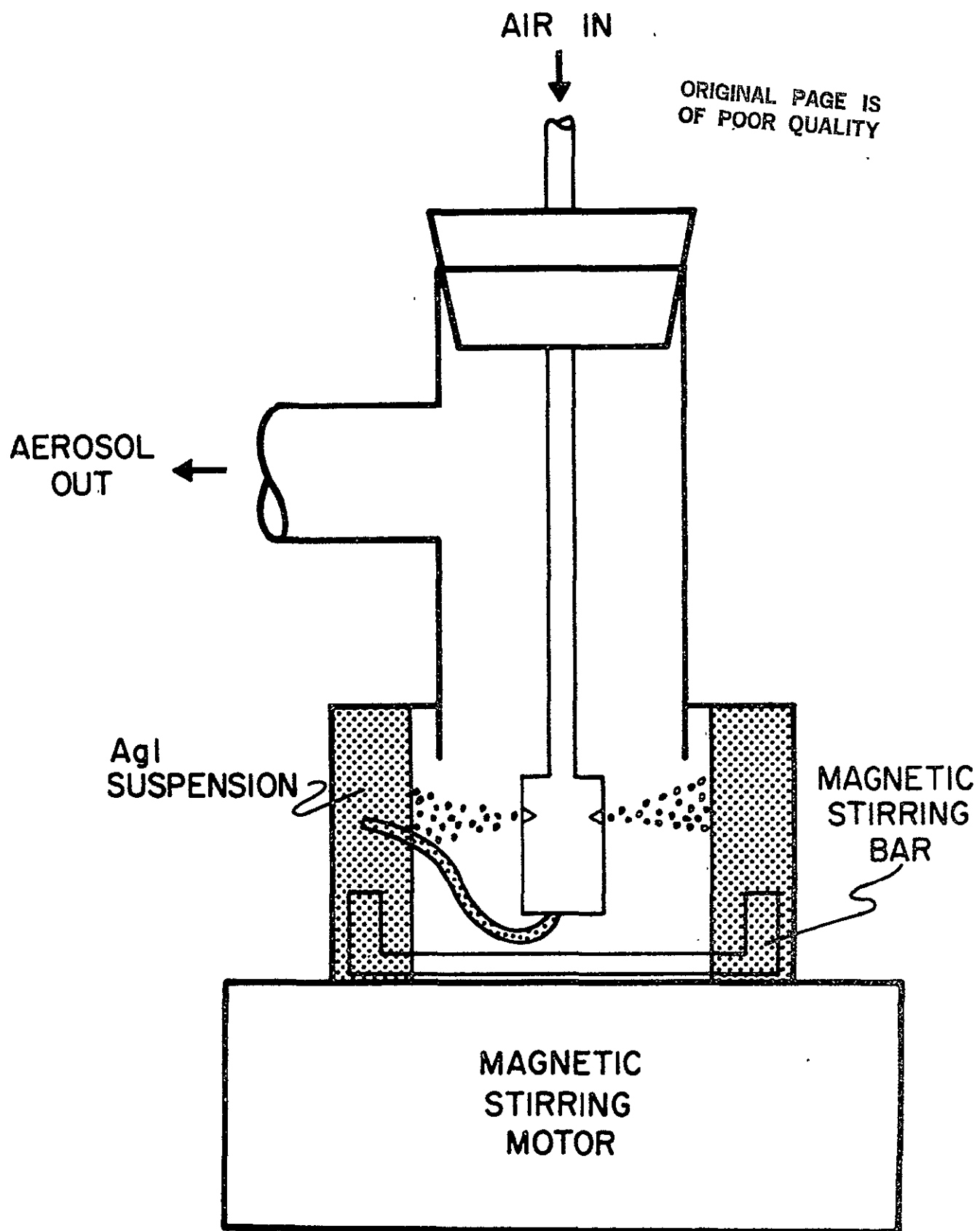


Fig. 4.A:1: Recommended adaptation of Collison nebulizer for use in low gravity environment.

The preparation of the liquid suspension has been described earlier in the report. The suspension could be precipitated prior to launch and stored for later use, but there would be a noticeable loss in particle concentration and changes in the hydrosol size distribution due to diffusion and sedimentation to the walls, coagulation and possible dissolution and chemical effects. For all of the nucleation studies in this report, the suspension was precipitated each experimental morning, and discarded the following morning; the day-to-day reproducibility was excellent. The small amount of concentrated solution (0.05 ml) and distilled water (200 ml) used in each batch did not warrant storage; perhaps the limitations of ACPL would change this practice.

The proportions of AgI-NH<sub>4</sub>I solution to distilled water for the precipitation stage of particle generation are not critical as long as the amount of distilled water is much larger than the silver iodide solution. This ensures that a large supersaturation is achieved and that a large number of particles form quickly. The subsequent growth of the nucleated particles continues until solute equilibrium is again reached. Thus, within the range of values which we tested, the effect of using more AgI-NH<sub>4</sub>I solution is to grow the same number of particles to a larger size. For convenience we selected the ratio of 0.05 ml AgI-NH<sub>4</sub>I complex to 200 ml distilled water. Any alteration of this ratio is expected to change both the size distribution and the nucleating activity of the aerosol.

It is our recommendation that a fresh batch of AgI suspension be precipitated each experimental day and that the excess suspension from the previous experiment be discarded. There are no difficulties or hazards expected in handling either the concentrated aqueous solution or the suspension. Scrupulous cleaning of the nebulizer between experiments is not necessary. It is

sufficient to remove the remaining used suspension by suction. Should clogging or accumulated residue become excessive, a concentrated solution of ammonium iodide will be required to dissolve the deposits. It should be mentioned that we encountered no clogging problems during this research; we typically rinsed the nebulizer with ammonium iodide followed by a distilled water rinse at the start of each experimental day. The concentrated ammonium iodide used for cleaning can be reused, and so the amounts of cleaning supplies and disposables are not excessive.



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note: JAM = Journal of Applied Meteorology  
 JAS = Journal of the Atmospheric Sciences

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## APPENDICES

### INSTRUMENTATION WORKSHOPS

The first instrumentation intercomparison workshop in support of the subject contract was held at the Desert Research Institute (DRI), Atmospheric Sciences Center, during September of 1977, and the second workshop was held at the University of Wyoming, Department of Atmospheric Science during March of 1978. The active participants were DRI and the University of Wyoming. In order to avoid redundancy in preparing reports on these workshops, the University of Wyoming and DRI agreed that the host institutions should prepare the separate workshop reports. Therefore, Appendix A was prepared by DRI and Appendix B was prepared by the University of Wyoming.

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VI. APPENDIX A

Instrumentation Workshop - Reno, Nevada

Detailed results from this workshop have been presented in Monthly Report No. 10 (Oct 28, 1977) of the Desert Research Institute under their contract No. NAS8-32313.

The conclusions given in that report were: "Results of the first workshop between DRI and the University of Wyoming were more than satisfactory in view of the complicated nature of the experiments, the widely different instruments that were used and the short time available to get everything working. Our objective for this preliminary workshop was to generate NaCl and H<sub>2</sub>SO<sub>4</sub> aerosols in the desired 0.01 to 0.1  $\mu$ m size range to compare, to the extent possible, the various aerosol analyzers.

"Suprisingly good agreement among instruments was observed in most tests. Perhaps the real benefit, however, was in the essential background experience that was gained which can now be used to design our follow-on experiments. With some added analysis of the data, we should be in a position to design a series of definitive comparisons for the next joint workshop".

Four main objectives were outlined for the workshop:

- 1) perform comparisons between the Electrostatic Classifier (EC), the Electrical Aerosol Analyzer (EAA), the CNC-2 and Gardner Counter for several different aerosols;
- 2) compare the measurements of the CFD and SDL CCN chambers;
- 3) determine the CCN activity of the AgI suspension aerosol using the different available equipment; and
- 4) examine the size dependence of ice nucleating activity of the AgI suspension aerosol using the DRI classifier and the Wyoming ice nucleus measuring instruments.

All of these objectives were met during the course of the workshop. Many straightforward experiments were performed; they will not be described in detail here, but the results will be discussed in the order listed above.

1) EAA comparison with EC, CNC-2 and Gardner Counter

The EAA and EC instruments utilize the size fractionating of aerosols according to electrical mobility, and they have rather similar physical characteristics and operating characteristics; they are both manufactured by Thermo-Systems, Inc. The CNC-2 and Gardner Counter, on the other hand, are expansion cloud chambers; they measure the extinction of light. The EC-EAA comparison consisted of generating a monodisperse aerosol with the EC and comparing that size with the size distribution indicated by the EAA. The EAA-CNC-2 and EAA-Gardner Counter comparisons were for total particle concentrations.

Several different aerosols were used for the comparisons, including NaCl from the COA and AgI suspension aerosol from the DeVilbiss and Collision

## VII. APPENDIX B

### Instrumentation Workshop - Laramie, Wyoming

#### Introduction

The second instrumentation workshop in support of the ACPL experiments was held in Laramie, Wyoming, at the facilities of the University of Wyoming, Department of Atmospheric Science during the week of 6 to 10 March 1978. The principal participants and their affiliations are listed below:

B. Black	University of Wyoming
G. Gordon	" " "
J. Hudson	Desert Research Institute, Reno
U. Katz	" " " "
G. Keyser	" " " "
W. Kocmond	" " " "
D. Rogers	University of Wyoming
G. Vali	" " "

The primary instrumentation which was used during the workshop consisted of equipment located at the University of Wyoming (the Wyoming Aerosol System, DFC ice nucleus instrument, SDL CCN chamber, Gardner Counter, aerosol generators and other components of the aerosol facility) as well as several instruments brought to Laramie from the Desert Research Institute (two CFD chambers, the prototype ACPL CFD and saturator, an Electrostatic Classifier and a Constant Output Atomizer COA). The better part of the first day was spent in assembling and checking out the DRI equipment and in formulating plans for the particular experiments of the workshop. It was gratifying to learn that the ordeals of disassembling, transporting 1200 miles and reassembling the DRI equipment did not prevent its proper functioning when tested.



nebulizers. Details of the generation process have been described in the main body of this report. After generation, the high concentration aerosol was diluted slightly (to match flow requirements) and fed to the EC. The 'monodisperse' fraction was output from the EC and fed into the EAA along with a sufficient amount of dilution air to match flows. The modal size of the 'monodisperse' aerosol was selected by adjusting the precipitating voltage and flow rates to predetermined values using the manufacturer's specifications.

A typical 'monodisperse' aerosol size distribution, as measured by the EAA, is given in Figure 1. The histogram depicts the actual measurement by the EAA channels (voltage steps) and the smooth curve represents our estimate of the true distribution. The single solid circle with error bars indicates the position of the modal value and the size of the half-width of the distribution.

The 'monodisperse' aerosol size distributions typically were of log-normal shape with geometric standard deviations of about half of the half-width. Thus, the region one half-width wide about the mode contained about 95% ( $2\sigma$ ) of the total number of particles. (This observation is a consequence of the shape of these measured spectra and is not true in general for log-normal distributions.)

The results of the first comparison, EC monodisperse size versus EAA measured size, are presented in Figure 2. The data points and error bars on the EAA diameters represent the modal sizes and widths of the differential size spectra at half the peak values, i.e., the half-widths. This plot indicates a very good correspondence between the two instruments. The correlation coefficient between these data is +.986, and the least-squares line is:  $EC = 1.15 EAA .997$ , suggesting that the EAA measures a modal size

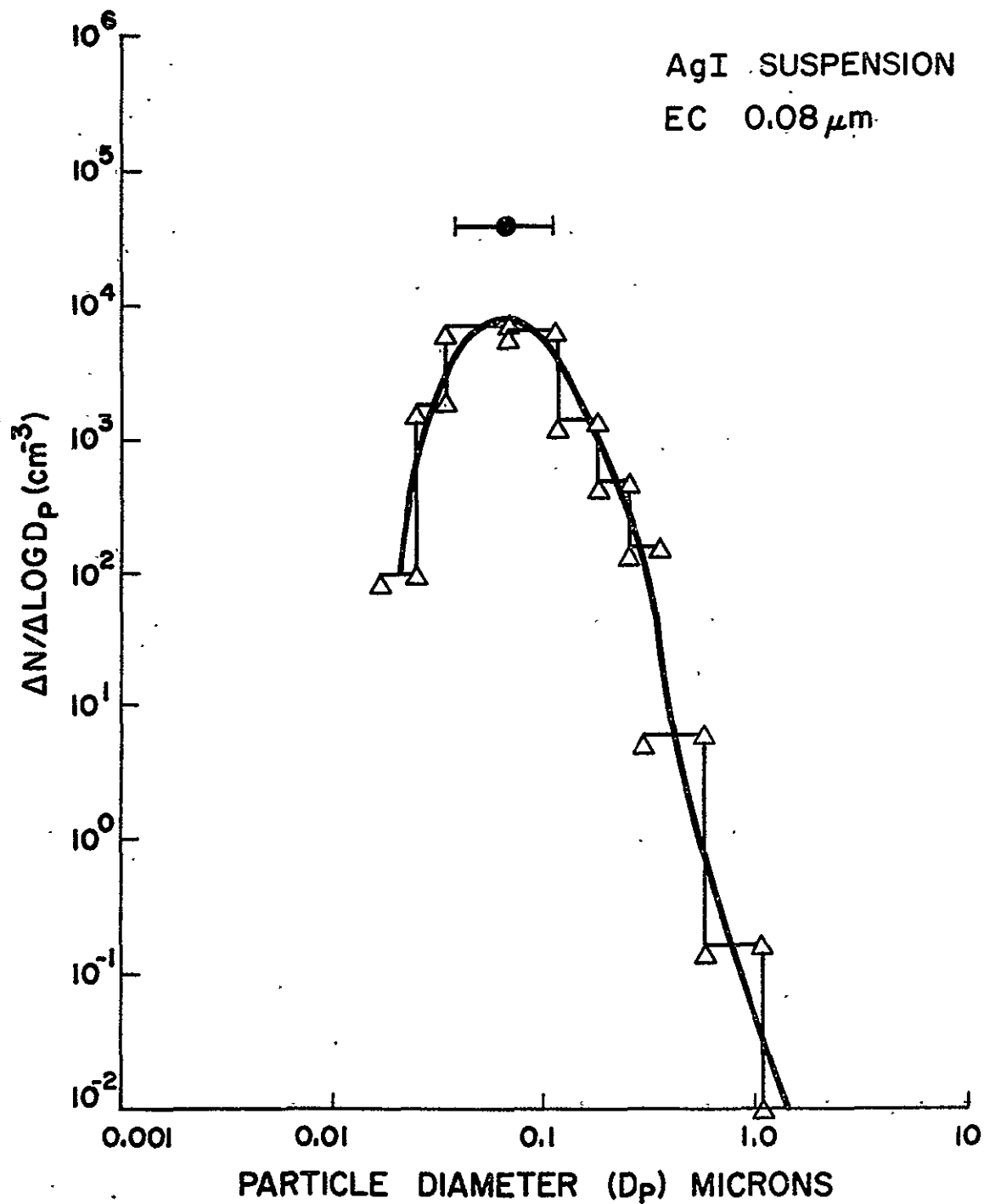


Figure 1. Typical size distribution for the AgI suspension aerosol, output from the EC as "monodisperse".

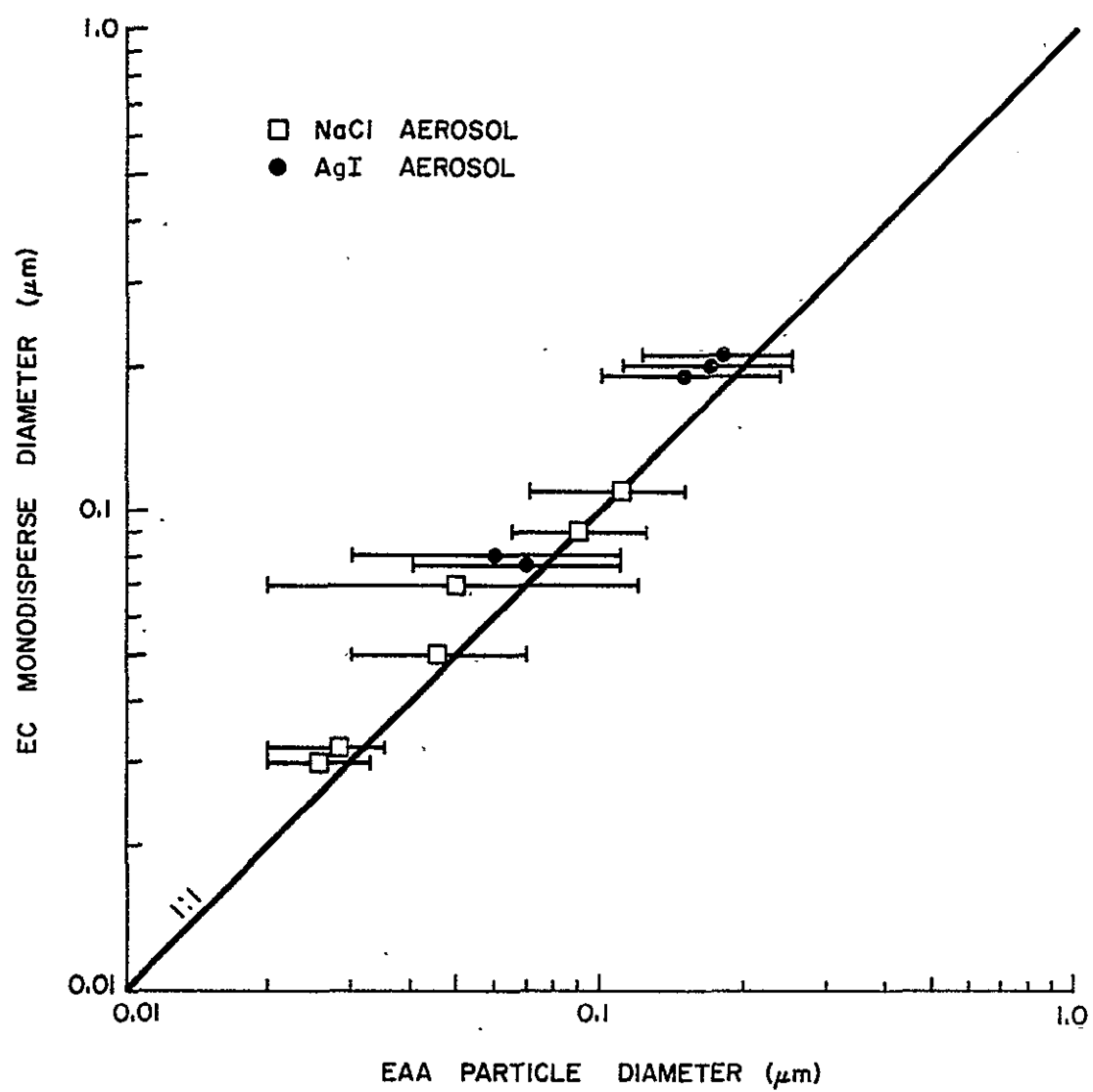


Figure 2. EC-EAA size comparison.

which is about 15% smaller than that determined from the EC flow and voltage calibration. A better comparison could be obtained if the resolution of the EAA were finer. The typical size spectra as measured by the EAA had 90% of the particles in two channels, so that the true shape of the spectrum in the region of the narrow peak is not well defined. This aspect is demonstrated in Figure 1.

The second comparison, that of total concentration, is given in Figure 3. This figure indicates that the EAA tends to give higher concentrations than either of the expansion chamber total particle counters. The discrepancy is worse for the Gardner counter than for the CNC-2. Several aerosols were used for these tests: room air, outside air, monodisperse NaCl (from the EC) and monodisperse and polydisperse AgI. There was no apparent trend for the different aerosols, so they were not distinguished in the figure. The CNC-2 and EAA agree to within a factor of two for 80% of the measurements. The data also suggest that the EAA tends to read higher for high concentrations and lower for low concentrations. This amount of agreement seems fairly good when viewed in the light that the instruments operate on two vastly different principles, they are sensitive to quite different aspects of the aerosols, and the EAA is operating near the lower limit of its sensitivity.

The disparity for the Gardner Counter, however, seems to be systematic, and may be due to the inability of this device to activate the smaller particles (less than about  $0.03 \mu\text{m}$  according to Walter and Jaenicke, 1975). When the Gardner measurements are compared with the EAA values for particles larger than  $0.03 \mu\text{m}$ , the agreement is substantially better.

## 2) Comparison between CFD and SDL CCN chambers

The operating principles for these two chambers are identical; they are both parallel-plate diffusion chambers which use a temperature difference



between the top and bottom plates to establish a supersaturation region in the center. The capabilities are substantially different because of the designs: the Continuous Flow Diffusion chamber will provide a continuous record of CCN concentrations active at the selected supersaturation; the temperature difference is maintained by two thermally regulated circulating baths so that changes in supersaturation to different values are not quickly realized. On the other hand, the Static Diffusion Liquid chamber has temperature control via thermoelectric coolers, and the chamber has relatively small thermal inertia so that changes to different supersaturations are accomplished quickly, typically in less than one minute. However, the SDL cannot give a continuous record since the sample must be stopped inside the chamber in order to be photographed. Thus, the CFD is well suited for monitoring concentrations at any one supersaturation and the SDL is well suited for obtaining activation spectra in a batch-wise mode.

Two CFD chambers were provided by DRI, so that activation spectra could be obtained with these devices operating at different supersaturations. The comparisons between the CFD's and the SDL were performed for several different criteria: concentrations at the same supersaturation, critical supersaturation for monodisperse aerosols of known composition, and shape of the CCN spectra for natural air samples and polydisperse AgI.

The results of the first comparison, concentration at the same supersaturation, are presented in Table 1. The data indicate that the CFD obtains values approximately 50% larger than the SDL over a wide range in supersaturations and concentrations and for several different aerosols. The consistency of the ratio, CFD/SDL, verifies that the chambers respond similarly to different particles. The difference in measured concentrations could have several causes, such as vapor depletion in the SDL or time-lags in activation causing the SDL to under-count, or others. The discrepancy between the two types of measurements does not appear to be a function of supersaturation.



TABLE 1. CFD-SDL Comparison

Aerosol	Supersaturation(%)	Concentration (no.cm <sup>-3</sup> )		CFD/SDL
		SDL	CFD	
room air	.28	95	168	1.77
	.36	207	288	1.39
	.50	164	219	1.34
	.65	243	352	1.43
	1.02	1310	3596	2.75
outside air	.35	320	241	0.75
polydisperse NaCl	1.00	327	497	1.52
polydisperse AgI	1.00	371	613	1.65
		368	544	1.48
monodisperse AgI (0.2 $\mu$ m dia.)	0.2	485	750	1.55
	1.0	485	810	1.67
		CFD/SDL		avg. $1.57 \pm .47$
				omitting 2 extremes, avg. $1.53 \pm .14$

The second comparison, critical supersaturation for monodisperse aerosols, used both NaCl and AgI aerosol. The EC was used to extract a selected monodisperse fraction from the polydisperse aerosol available from the generator. The appearance of the CCN spectra was rather like step functions, so that no drops were detected until a value of  $S_c$  was reached, and increases in supersaturation beyond  $S_c$  did not add noticeable numbers of droplets. The technique was to increment the supersaturation from less than to greater than the critical value and to note when droplets first appeared in large numbers. The results of this comparison are presented in Table II. Notice the excellent agreement between the instruments and between the instruments and the theoretical predictions (based on Kohler theory, see for example, Mason, 1971, chapter 1).

TABLE II. Critical supersaturation.

Aerosol	Critical Supersaturation (%)		Theory
	SDL	CFD	
NaCl .03 $\mu\text{m}$ dia.	.36	.32	.35
NaCl .05 $\mu\text{m}$ dia.	.75	.68	.75
Agl-NH <sub>4</sub> l complex 0.2 $\mu\text{m}$ dia.	< 0.2	< .25	.07

The good agreement serves to verify the accuracy of the temperature measurements, the assumptions about the vapor and temperature diffusion fields in the chambers, the aerosol generation and measurement accuracy and the nucleation theory.

The final comparison between these instruments involved comparing the measured shapes of CCN spectra for several different aerosols. This comparison is summarized in Figure 4 with four sets of paired CCN measurements. The discrepancy in concentration which was shown in Table I is also apparent in this figure. The slopes in the spectra are similar, although there are not enough paired measurements to make this slope comparison quantitative. The spectrum labelled "outside air 10 March" demonstrates that the aerosol occasionally changed with time; in this case, the CFD measurements at 1% changed by a factor of two during the period when the SDL was measuring the spectrum. This problem was not as serious for the lab-generated aerosols, where the concentration was either very steady over periods of an hour or more (from a steadily operating generator) or was decaying at a slow and steady rate (as in a storage bag with diffusion and coagulation losses). The outside air spectra measured were quite typical of a continental springtime aerosol, with C-values of 500 to 1000  $\text{cm}^{-3}$  and slopes (k-values) ranging from 0.2 to 1.1.

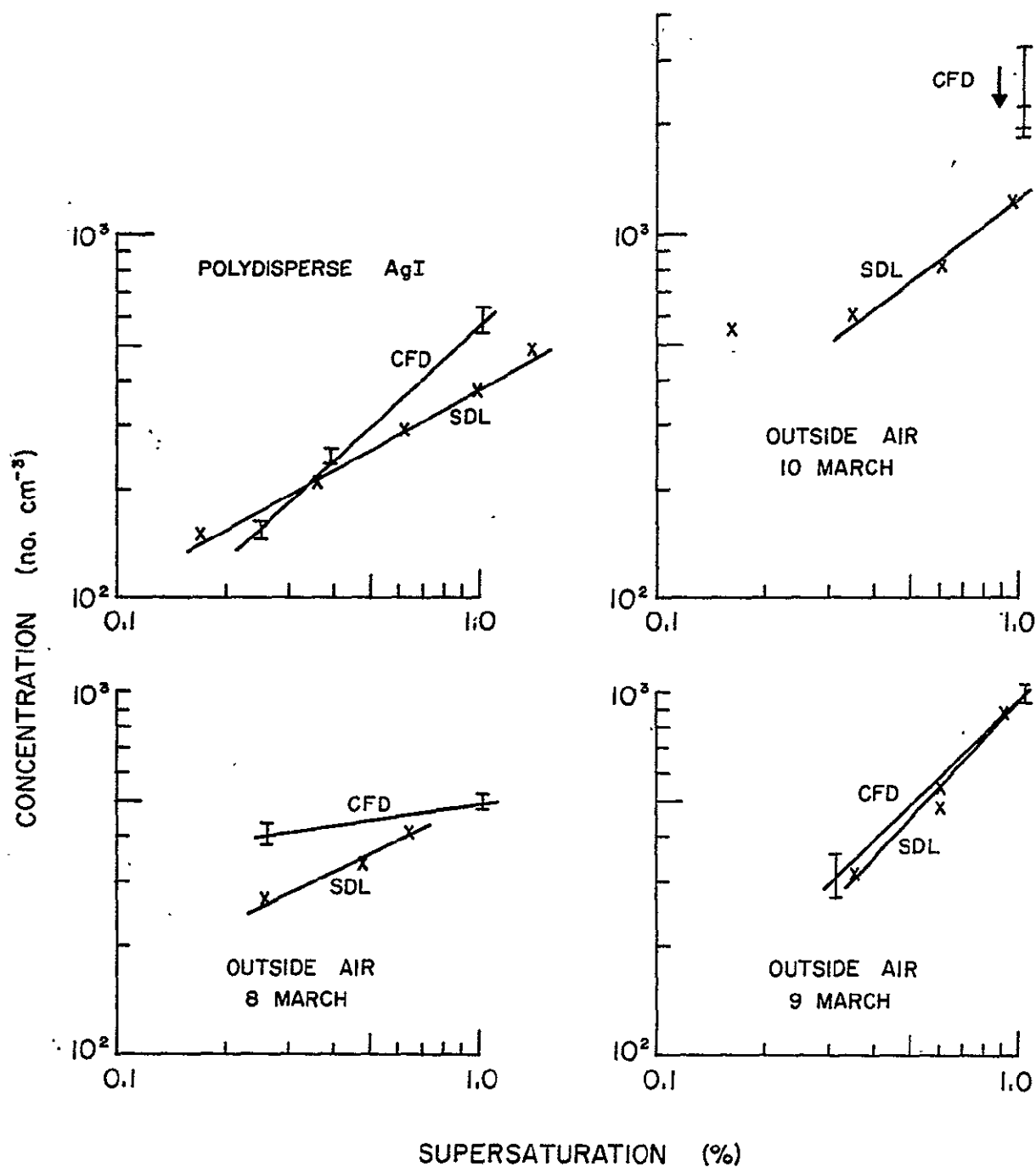


Figure 4. CCN spectra.

### 3) CCN activity of the AgI suspension aerosol

This objective was of fundamental importance to the University of Wyoming's effort to characterize the ice nucleating aerosol in terms of its ability to nucleate both ice and liquid phases. For these measurements, the AgI-NH<sub>4</sub>I complex suspension aerosol was generated with the Collison atomizer, and it was diluted and dispersed and transported inside the three inch metal duct which supplied aerosol samples to the CFD, the SDL and the Wyoming Aerosol System. The size distribution of this aerosol was very reproducible for this arrangement, a typical size plot can be found in Figure 4.A.3 of the Final Report.

As elaborated in the Final Report, during the generation process the aerosolized droplets consist of weak aqueous solutions of NH<sub>4</sub>I and suspended AgI particles. As the droplets evaporate, the concentration of NH<sub>4</sub>I increases to the point where some of the AgI is dissolved, and as evaporation continues a complex of AgI-NH<sub>4</sub>I precipitates. Thus, the final dry aerosol probably consists mostly (depending on its initial size) of AgI with smaller regions of AgI-NH<sub>4</sub>I complex and perhaps some NH<sub>4</sub>I in an uncombined form. Both AgI-NH<sub>4</sub>I and NH<sub>4</sub>I are hygroscopic; the deliquescence point for NH<sub>4</sub>I is about 89% relative humidity. Thus the aerosol is expected to be a very active liquid condensation nucleus (this is in substantial contrast with pure AgI which is hydrophobic).

The activation spectrum for the polydisperse AgI aerosol is given in Figure 4 for measurements by both the CFD and SDL instruments. The theoretical expectation for the activation spectrum of an aerosol of pure NH<sub>4</sub>I having the size distribution of the polydisperse AgI suspension would parallel the CFD curve and lie approximately a factor of 1.2 smaller in supersaturations. This result is expected because of the mixed chemical nature of the particles; pure NH<sub>4</sub>I is expected to activate at lower supersaturations. The close agreement

(factor of 1.2) indicates that these particles are well behaved, from the point of view of condensation theory.

The activity of the AgI suspension aerosol in Figure 4 and in Tables I and II indicates that indeed the particles are quite active as condensation nuclei. This characteristic allows considerable leeway in the design of ice nucleation experiments for the ACPL, since the aerosol can be used with good predictability for both the cloud-forming and ice-forming parts of an experiment, if desired. The liquid condensation potential of the aerosol is uniquely related to the size distribution through condensation theory, and the ice forming potential was shown in the Final Report to be uniquely related also to the aerosol size distribution (more specifically, the distribution of surface area).

#### 4) Size dependence of nucleation for AgI suspension aerosol

The simultaneous presence of both the EC (from DRI) and the Wyoming ice nucleation instruments made possible a series of experiments to examine the nucleating ability as a function of aerosol size. For these experiments, the high concentration AgI suspension aerosol from the Collison nebulizer was fed into the EC, and a monodisperse fraction of preselected size was extracted. This was then fed under pressure into the main aerosol distribution duct. The resulting total particle concentration was reduced from about  $10^6 \text{ cm}^{-3}$  at the generator to about  $10^3 \text{ cm}^{-3}$  in the duct. This concentration was within the range of all of the various sampling instruments (DFC, CFD, SDL, CNC-2 and the Wyoming Aerosol System). A typical size distribution for the "monodisperse" AgI suspension aerosol has been presented in Figure 1. The results of the nucleation tests are presented in Table III for two different temperatures. The concentration at the generator was calculated by multiplying the measured ice nucleus concentration by the ratio, Aitken particle concentration at

generator/Aitken measurement in duct. Two trends are evident in Table III: first, the larger particles are more active at the same temperature, and second, activity for the same monodisperse aerosol falls off rapidly with warmer temperatures (factor of three less active at  $-8^{\circ}\text{C}$  than  $-10^{\circ}\text{C}$  for  $0.2\text{ }\mu\text{m}$  particles). As a result of this demonstration of dependence of activity upon size, further experiments were undertaken after the workshop. These more extensive results are contained in the Final Report.

TABLE III. Nucleation tests on classified AgI aerosol

Temperature	Aerosol	Active Fraction	Concentration (per liter) at generator
-10	polydisperse	$3.0 \times 10^{-6}$	2200
-10	$0.2\text{ }\mu\text{m}$ monodisperse	$1.4 \times 10^{-5}$	10,000
-10	$0.08\text{ }\mu\text{m}$ monodisperse	$4.5 \times 10^{-6}$	3300
-8	$0.2\text{ }\mu\text{m}$ monodisperse	$4.6 \times 10^{-6}$	3400

### Conclusions

The second ACPL instrument evaluation workshop led to the following conclusions:

1. The COA generator - EC combination was shown to be a sufficient and practicable way for generating monodispersed aerosols from solution.
2. With some apparent loss in size resolution, the EAA agreed with the EC on the concentration and modal sizes of aerosols. These results are quite encouraging for the planned use of these instruments in the ACPL, although the accuracy of the measurements is indicated in these tests to be about  $\pm 10\%$ .

3. The CNC-2 and the EAA measured total particle concentrations within about a factor 2 discrepancy.
4. The CFD and SDL chambers were shown to agree on the set values of the supersaturation within the chambers to better than  $\pm 0.05\%$  in S.
5. The SDL device indicated about a factor 1.5 lower concentrations of CCN than the CFD. This is believed to be due to limitations in the SDL operating principle.

#### References

- Mason, B. J., 1971: The Physics of Clouds, Clarendon Press, Oxford, 671 pp.
- Walter, H. and R. Jaenicke, 1973: Remarks about the smallest particle size detectable in condensation nuclei counters. Atmos. Environ. 7, 939-944.